Insertion of Terminal and Internal Acetylenes into the Zr−μ-Methylene Bond of the Dinuclear Cationic Zirconium Complex [{Zr(η^5-C_5H_5)}$_2$(μ-CH_2)(μ-Cl)(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$]. Synthetic Aspects, NMR Spectroscopic Study, and Dynamic Behavior in Solution

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The dinuclear cationic zirconium species [{Zr(η^5-C_5H_5)}$_2$(μ-CH_2)(μ-Cl)(μ-η^5-C_5H_4-η^5-C_5H_4)]-[BMe(C_6F_5)$_3$] (**1**) reacts in dichloromethane at −78 °C with terminal alkynes, via insertion into the Zr−μ-methylene bond, to give various dinuclear cationic derivatives. Reaction of **1** with $Me_3SiC{\equiv}CH$ gives the hydrido complex [{Zr(η^5-C_5H_5)}$_2$(μ-Cl)(μ-H)($CH_2C{\equiv}CSiMe_3$)(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$] (**2**)**,** whereas 1-pentyne and 3,3-dimethyl-1-butyne give the μ-η^1-η^3-(2-alkyl)allyl derivatives [{Zr(η^5-C_5H_5)}$_2$(μ-Cl){μ-[η^1-η^3-CHC(^{n}Pr)CH_2]}(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$] (**3**) and [{Zr(η^5-C_5H_5)}$_2$(μ-Cl){μ-[η^1-η^3-CHC(^{t}Bu)CH_2]}(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$] (**4**). Compounds **3** and **4** show dynamic behavior in solution involving an interchange between two enantiomeric structures through a suprafacial migration of the "−RC=CH_2" moiety. When compound **1** was treated with a molar equivalent of internal alkynes RC≡CR (R = Et, ^{n}Pr), formation of [{Zr(η^5-C_5H_5)}$_2$(μ-Cl){μ-CH_2C(Et)=C(Et)}(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$] (**5**) and [{Zr(η^5-C_5H_5)}$_2$(μ-Cl){μ-CH_2C(^{n}Pr)=C(^{n}Pr)}(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$] (**6**) was observed, which were isomerized to the [{Zr(η^5-C_5H_5)}$_2$(μ-Cl){μ-CH_2C(Et)CH=CHMe}(μ-η^5-C_5H_4-η^5-C_5H_4)] [BMe(C_6F_5)$_3$] (**7**) and [{Zr(η^5-C_5H_5)}$_2$(μ-Cl){μ-CH_2C(^{n}Pr)CH=CHEt}(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$] (**8**) derivatives at room temperature, through a β−α hydrogen migration. The new complexes reported were characterized by elemental analysis and IR and NMR spectroscopy.

Introduction

The formation of dinuclear compounds has been invoked[1a,2,3] as an important step in the deactivation of alkene polymerization catalysts based on the known[4] active d^0 cationic group 4 metallocene compounds $[MCp_2R]^+$ (M = Ti, Zr, Hf), generated from the reaction of Lewis acid cocatalysts [AlR_3, MAO, $B(C_6F_5)_3$] with the precursor metallocenes MCp_2R_2. Besides the involvement of the cationic d^0 species $[MCp_2RL]^+$ as homogeneous catalysts in alkene polymerization processes, much work has also been devoted to the reactivity of these mononuclear 14-electron cations with CO, RNC, olefins, acetylenes, or allenes to give novel organome-

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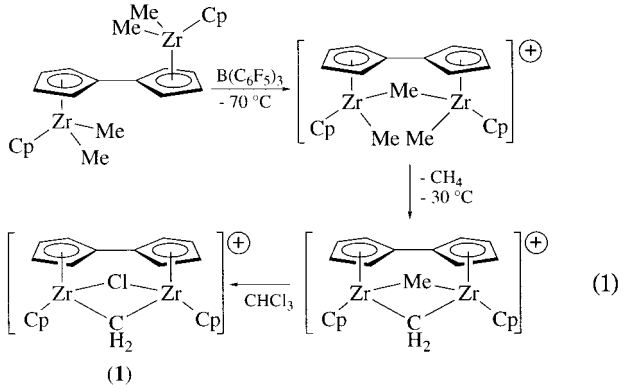
tallic compounds.[5−7] However, cationic homo- and hetero-dinuclear group 4 metal compounds have received less attention[1] despite their significance in polymerization processes[1b] and in many other heterogeneous C−H activation and C−C bond formation catalytic reactions.[8]

Novel dinuclear cationic zirconium complexes prepared from dialkynyl zirconocene derivatives have been reported as interesting reagents for stoichiometric and catalytic reactions.[1e,9] The isolation of dinuclear group 4 metal compounds containing a bridging fulvalene ligand has received increasing interest in the past few years.[10] The bridging ligand allows the metal fragments to be disposed either cis or trans with respect to the fulvalene plane, depending on electronic and steric factors. It also renders short distances between the metal atoms when they adopt the cis position, allowing additional bridges to form and even participating in weak metal−metal interactions. Such compounds, which contain two proximal electron-deficient metal centers, provide potential model systems to evaluate how the participation of both metals can modify the reactivity patterns exhibited by the corresponding mononuclear compounds.

Although different insertion reactions into the alkylidene bridging group have been reported[11] for middle and late transition metal complexes, studies concerning the reactivity of the "Zr−CH_2−Zr" fragment are limited due to its inaccessibility. Some heterodimetallic Zr−Th and Zr−Al derivatives containing the μ-CH_2 unit are known.[12] We reported[3a] the immediate and quantitative formation of the red μ-CH_2 cationic species [{Zr(η^5-C_5H_5)}$_2$(μ-CH_3)(μ-CH_2)(μ-η^5-C_5H_4-η^5-C_5H_4)]$^+$ (eq 1) by reaction of the tetramethyl zirconium fulvalene complex [Zr(η^5-C_5H_5)(CH_3)$_2$]$_2$(μ-η^5-C_5H_4-η^5-C_5H_4)] with [CPh_3][$B(C_6F_5)_4$] or $B(C_6F_5)_3$ in dichloromethane at −60 °C. The reactions of this cationic species with donor ligands and chlorocarbon solvents have been studied, and the formation of the μ-chloro μ-methylene fulvalene cationic compound [{Zr(η^5-C_5H_5)}$_2$(μ-CH_2)(μ-Cl)(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$] (**1**)[3b] was observed.



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In this paper we report on the results observed when different terminal and internal alkynes are inserted into the "Zr−CH_2−Zr" fragment of the cationic μ-methylene zirconium compound **1** and the structural characterization of the resulting products by elemental analysis and IR and NMR spectroscopic methods.

The reactivity of the μ-methylene compound **1** with alkynes is particularly important in relation to the mechanism of polymerization reactions. Titanium-initiated acetylene polymerizations seem to follow an insertion mechanism similar to that proposed for the group 4 metal catalyzed polymerization of α-olefins, which involves vinylidene intermediates, in contrast with the olefin metathesis processes observed in acetylene polymerizations catalyzed by molybdenum compounds.[13] The results reported here demonstrate that the reaction of the μ-methylene compound **1** with alkynes proceeds with insertion of the acetylene into a metal−carbon single bond; the regiochemistry of the addition is attributed to the polarity and steric demands of the alkyne substituents. We are also currently investigating the reactions of **1** and similar cationic derivatives with other unsaturated organic molecules.

Results and Discussion

Insertion of Terminal Alkynes. The reaction of a dichloromethane solution of [{Zr(η^5-C_5H_5)}$_2$(μ-CH_2)(μ-Cl)(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$][3b] (**1**) with $Me_3SiC{\equiv}CH$ at −78 °C in a 1:1 molar ratio gave the unusual hydrido-alkyl complex [{Zr(η^5-C_5H_5)}$_2$(μ-Cl)(μ-H)($CH_2C{\equiv}CSiMe_3$)(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$] (**2**), which was isolated as a yellow-orange solid in 84% yield after stirring the reaction mixture for 30 min at 0 °C and evaporation of the solvent (Scheme 1). The use of an

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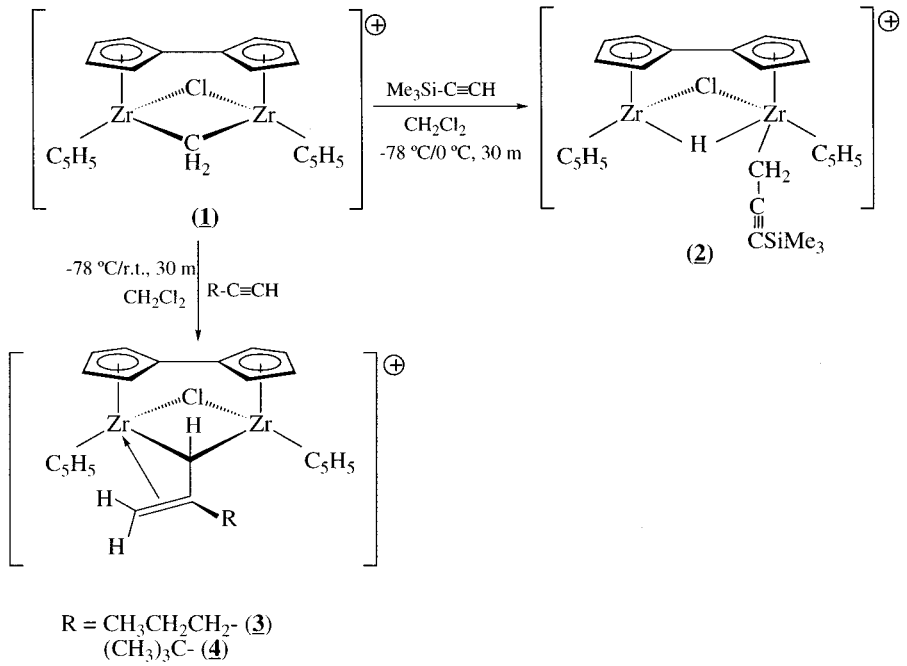
Scheme 1



excess of acetylene led to an unresolvable mixture of final products. Complex **2** is stable at low temperature but unstable at room temperature in solution and in the solid state. It is soluble in CH_2Cl_2 and $CHCl_3$ but insoluble in alkanes and aromatic hydrocarbons. Its IR spectrum showed characteristic absorptions corresponding to the ν(Zr−H−Zr) (1150 cm^{-1}) and ν(C≡C) (1950 cm^{-1}) vibrations.[6a,14]

The ^1H NMR (CD_2Cl_2, 223K) spectrum of **2** exhibited two ABCD spin systems for the fulvalene protons, two signals for the Cp rings, one singlet for $SiMe_3$ protons, and an ABX spin system for a "*CH_2−Zr−(μ-H)*" moiety, indicating the presence of two nonequivalent chiral zirconium atoms in the molecule. The ABX spin system is formed by two diastereotopic CH_2 protons at δ 2.97 and δ 2.44 ($^2J_{A-B}$ = 9.9 Hz) and one bridging hydride ligand at δ −4.67. The value of the vicinal proton−proton coupling constant ($^3J_{A-X} = {}^3J_{B-X}$ = 1.5 Hz) indicates that both groups (CH_2 and H) are bonded to the same metal atom.

The $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 223 K) spectrum of complex **2** is in accord with an asymmetric complex with one singlet observed for the methylene (CH_2) carbon atom at δ 37.2, reflecting the diamagnetic influence of the carbon−carbon triple bond, and two resonances observed for the sp carbon atoms (C≡C) at δ 104.2 and 115,2 slightly deshielding with respect to the expected range for acetylenes with known α- and β-silicon effects[15] but consistent with values found for zirconium-bound alkyl[6a,d] and propargyl ligands.[6d,16] The very strong shielding of the ^1H and ^{13}C resonances for CH_2, compared with **1**[3b] [$\Delta\delta_{av}(^1H)$ = 4.85 ppm and $\Delta\delta(^{13}C)$ = 163.7 ppm] is consistent with the loss of the bridging CH_2 ligand present in the precursor complex **1**, and these observations along with the analytical data permit us to formulate **2** as a dinuclear μ-H, μ-Cl double-bridged monoalkyl dinuclear cation.

Reaction of **1** with RC≡CH [R = $CH_3-CH_2-CH_2-$; $(CH_3)_3C-$] in dichloromethane at −78 °C gave the double-bridged complexes [{Zr(η^5-C_5H_5)}$_2$(μ-Cl){μ-η^1-η^3-CHC(^{n}Pr)CH_2}(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$] (**3**) and [{Zr(η^5-C_5H_5)}$_2$(μ-Cl){μ-η^1-η^3-CHC(^{t}Bu)CH_2}(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$] (**4**) (Scheme 1) as yellow-orange solids in 70−75% yield after the reaction mixture was warmed to room temperature and stirred for 30 min. However mixtures of **1**+**3** or **1**+**4** were obtained respectively when reactions with 1-pentyne or *tert*-butylacetylene were carried out at room temperature or in the presence of Lewis bases. When an excess of acetylene was used, unresolvable mixtures of final products resulted. Complexes **3** and **4** are stable at room temperature under an inert atmosphere and can be stored for weeks. They are soluble in CH_2Cl_2 and $CHCl_3$ but insoluble in alkanes and aromatic hydrocarbons. The most remarkable datum observed in the IR spectra of **3** and **4** is the characteristic absorption corresponding to the ν(C=C) (≈1500 cm^{-1}) vibrations.

The NMR spectra of the dinuclear cationic complexes **3** and **4** in CD_2Cl_2 are temperature dependent, with broad signals at room temperature, indicating a spin exchange process between the Cp ring signals and the corresponding resonances of the fulvalene system.

The ^1H NMR spectra of these dinuclear cationic complexes at 203 K show two signals for the Cp ring, two well-resolved ABCD spin systems for the fulvalene ligand, and an ABX spin system characteristic of a 2-R-allyl ligand[5] (see Experimental Section) in which the μ-C*H* and one of the two terminal CH_2 protons are located in a "W" disposition, consistent with the measured ^4J = 3.9 Hz (**3**) and ^4J = 3.5 Hz (**4**). The ^{13}C NMR (CD_2Cl_2) spectra at 203 K exhibit 10 resonances for the

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fulvalene ligands, two signals for the Cp rings, and resonances at δ 154.4 ($^1J_{C-H}$ = 111.6 Hz), 164.8, 62.9 ($^1J_{C-H}$ = 147.1 Hz) (**3**), and 146.4, 182.7, 42.4 (**4**) for the "$-CH-CR{=}CH_2$" moiety. The deshielded resonances around 165−185 ppm are attributed to the central carbon atom, and the shielded signals around 42−63 ppm are attributed to the terminal carbon and are characteristic of an η^3-allyl coordination.[6a,b,7] The chemical shift of the other terminal allylic carbon is deshielded with respect to typical terminal allylic carbon resonances and is therefore diagnostic of a σ Zr−C interaction.[11a,b]

These data are in agreement with the absence of any symmetry in the ground state (see Scheme 1), and the bonding in **3** and **4** may be described as a new type of zirconium μ-η^1-η^3-(2-alkyl)allyl interaction in which one terminal carbon−hydrogen bond has been replaced by a carbon−zirconium bond (or alternatively as a μ-η^1-η^3-vinylalkylidene zirconium coordination mode) with the "$-C(R){=}CH_2$" moiety located in the exo-position (outside) due to steric factors and the π-olefin orbitals interacting with the d-orbital ($2a_1$) of one zirconium center. The formation of mononuclear η^3-vinylcarbene metallocene complexes of electron-poor metals has been ruled out, in the literature, due to steric reasons.[17]

Attempts to obtain crystals for **2**−**4** suitable for X-ray crystallography studies were unsuccessful, and the crystallographic confirmation of the proposed structures was not possible. ^{19}F NMR spectra were recorded for all of the cationic complexes described in this report, but the data are unexceptional, and similar to other cationic derivatives with no cation−anion interaction, the $\Delta\delta$(*m*-, *p*-F) values are below 2.5 ppm.[4j]

Interconversion of the "−CR═CH$_2$" Moiety in 3 and 4. The observed dynamic behavior for **3** and **4** in CD_2Cl_2 solution requires an interchange between two enantiomeric structures; see Figure 1. Assuming C_1 symmetry for the ground state, C_s symmetry is proposed for the transition state.

Two different mechanisms may be, a priori, proposed to explain the enantiomerization process in the cationic complexes **3** and **4**. Antrafacial or suprafacial migration of the "$-CR{=}CH_2$" moiety from one zirconium atom to the other by oscillating around the "HC−CR" single bond of the bridging ligand would give two possible transition states, **i** and **ii**, respectively. Transition state **i** is characterized by the loss of the d−π metal−olefin interaction and of the "W" disposition of allyl protons (see Newman projection **i**) and may be described as a simple bridged μ-CH−C(R)═CH$_2$ group. Moreover, the change of this coordination mode must be reflected in a significant negative variation of $\Delta S^{\ddagger}$. Transition state **ii** may be described as a double-bridged allyl group formed by an interaction between the olefin π-bond and the d-orbitals of both zirconium atoms, in which the "W" disposition of allyl hydrogen (see Newman projection **ii**) is maintained. This is consistent with the $^4J_{H-H}$ coupling, corresponding to the "*W*" feature, observed in the variable-temperature NMR spectroscopic study (see Figure 2). This coordination mode change must proceed without a variation in the entropy factor.

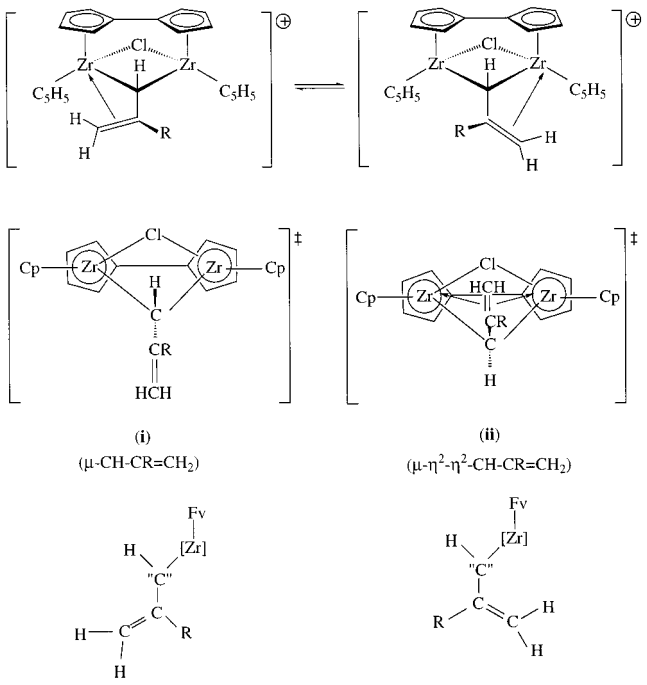


Figure 1. Enantiomerization process observed for compunds **3** and **4** in CD_2Cl_2 solutions.

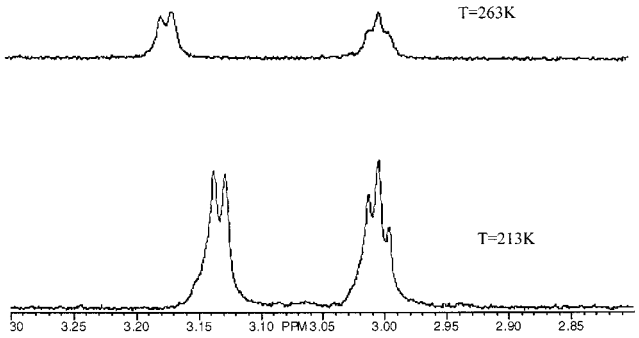


Figure 2. Resonances of the terminal "═CH$_2$" group in the enantiomerization process observed for compounds **3** and **4** in CD_2Cl_2 solutions.

We suggest, therefore, that the observed dynamic behavior involves the suprafacial interconversion of the "$-CR{=}CH_2$" moiety and must be characterized by similar entropy values in the ground and transition states.

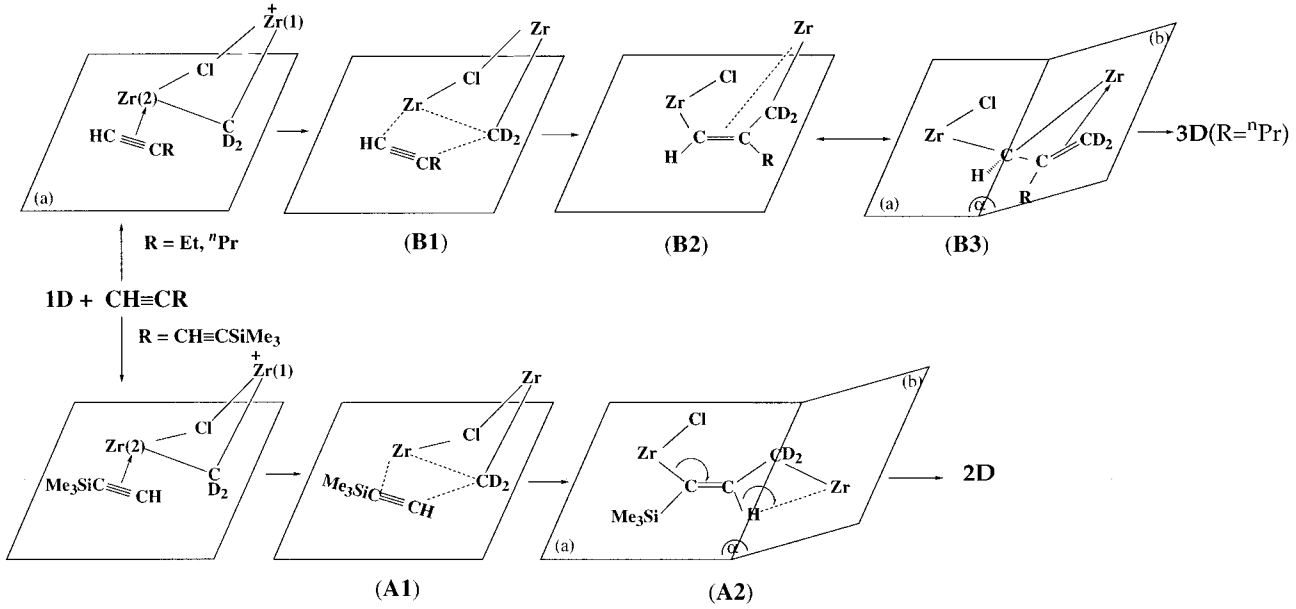
The kinetic parameters (Table 1), calculated for the mutual exchange of the Cp ring resonances by full line shape analysis, are consistent with a typical intramolecular process (log $A \approx 13$). The null variations of entropy factor ($\Delta S^{\ddagger}$) in both cases are in accordance with our proposal (transition state **ii**), the activation parameters (E_a, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$) being dependent on the volume of the C_2 alkyl substituent in the bridging ligand.

To the best of our knowledge, this is the first example of the suprafacial interconversion of an olefin moiety. This contrasts with the fluxionality exhibited by a variety of dinuclear carbenium complexes containing (μ-η^2,η^3-RC≡C−CR$_2$) ligands, in which the interconversion of the terminal CR_2^+ group takes place without any change in the coordination mode of the C≡C moiety.[18]

(17) (a) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149. (b) McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T. S.; Tebbe, F. N. *J. Am. Chem. Soc.* **1981**, *103*, 5584. (c) Beckhaus, R.; Sang, J.; Wagner, T.; Ganter, B. *Organometallics* **1996**, *15*, 1176.

(18) Amouri, H. E.; Besace, Y.; Vaissermann, J.; Jaouen, G.; McGlinchey, M. J. *Organometallics* **1994,** *13*, 4426.

Scheme 2



Planes (a) and (b) symbolize the bent metallocene wedges for Zr(1) and Zr(2) respectively; α denotes the angle between both planes

Table 1. Kinetic Parameters for Cp Ring Spin Exchange for Complexes 3 and 4 in CD_2Cl_2

complex	interval *T*, K	log *A*	E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger 298K}$, kcal/mol
3	243−298	13.2 ± 0.3	12.2 ± 0.37	11.7 ± 0.36	0 ± 1.2	11.7
			r = 0.9985		r = 0.9983	
4	253−288	13.0 ± 0.2	13.9 ± 0.2	13.4 ± 0.25	−0.9 ± 0.9	13.1
			r = 0.9992		r = 0.9990	

Mechanistical Proposal about the Insertion of Alkynes into the $Zr_2(\mu\text{-}CH_2)$ Bond. To obtain more information about the insertion of alkynes into the Zr−μ-methylene bond of cationic zirconium complexes, we have synthesized the deuterium-labeled initial complex **1D**, by reacting [{Zr(η^5-C_5H_5)(CD_3)$_2$}$_2$(μ-η^5-C_5H_4-η^5-C_5H_4)] with $B(C_6F_5)_3$ in $CHCl_3$, and studied subsequent reactions with the acetylenes RC≡CH (R = $SiMe_3$, ^{n}Pr). The CD_2-labeled complex [{Zr(η^5-C_5H_5)}$_2$(μ-CD_2)(μ-Cl)(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$] (**1D**) reacted with $SiMe_3C$≡CH to afford [{Zr(η^5-C_5H_5)}$_2$(μ-Cl)(μ-H)(CD_2C≡CSiMe_3)(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe(C_6F_5)$_3$] (**2D**) [^{2}H NMR (500 MHz, CD_2Cl_2): δ 2.97, 2.44 CD_2C≡CSiMe_3; 0.50 (br) CD_3B], and with ^{n}PrC≡CH to give [{Zr(η^5-C_5H_5)}$_2$-(μ-Cl)(μ-η^1:η^3)(CHC(^{n}Pr)=CD_2)(μ-η^5-C_5H_4-η^5-C_5H_4)][BMe-(C_6F_5)$_3$] (**3D**) [^{2}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 3.20, 2.90 (CHC(^{n}Pr)=CD_2); 0.50 (br) CD_3B].

The observed behavior of the "*Zr−CH$_2$−Zr*" unit in the reactions with alkynes can be rationalized by accepting that electronic and/or steric effects are responsible for the regiospecificity of the insertion process.

It is likely that the first step of the reaction of complex **1D** with the RC≡CH reagents involves the intermediate formation of a species containing the alkyne coordinated to one of the zirconium atoms. This then facilitates the formation of a coplanar four-center intermediate in which alkyne addition takes place. Our results suggest that the orientation of the alkyne substituents represented by **A1** in Scheme 2 dominates for Me_3SiC≡CH due to polarization in the C≡C triple bond. This favors coordination of the silyl-bound carbon with a higher electron density to the metal center,[15] despite the higher steric congestion between the Cp ligand and the rather bulky silyl substituent. However the **B1** orientation is preferred by the RC≡CH (R = ^{n}Pr, ^{t}Bu) alkynes which are characterized by low polarization in the C≡C triple bond; the **B1** orientation is adopted mainly for steric reasons. Consequently the subsequent methylene 1,2-addition for the silyl acetylene **A2** takes place, while a 2,1-addition is favored for the alkyl acetylenes **B2**, in which the chlorine bridge is broken, and in both cases a bridging three-carbon chain and a cationic Zr(1) center is formed. Mononuclear titanocene vinylidene intermediates react with alkynes[15] or 1,3-diynes[19] with insertion into the Ti=C double bond to give planar titanacyclobutenes. Similarly, **A2** may form a planar "*Zr(2)−C(SiMe$_3$)C=CHCD$_2$*" unit with the μ-propene ligand resulting from insertion of the alkyne into a Zr−C single bond of the μ-methylene ligand in the dinuclear fulvalene complex **1D**. With this **A2** disposition favored by the flexibility of the fulvalene ligand which causes a slight rotation around the central carbon−carbon single bond, and the availability of the chlorine atom to adopt a terminal or a bridging disposition,[20] transfer of hydrogen to the zirconium atom (Zr(1)) by β-elimination may be possible since the hydrogen is in the required orientation to allow subsequent β-elimination to give the hydrido-alkyl, which further rearranges to the bridging hydrido species **2D**. The thermal lability of this compound, which decomposes at temperatures higher than 0 °C, may be associated with the easy reductive elimination of alkane from its hydrido-alkyl ligands. The IR

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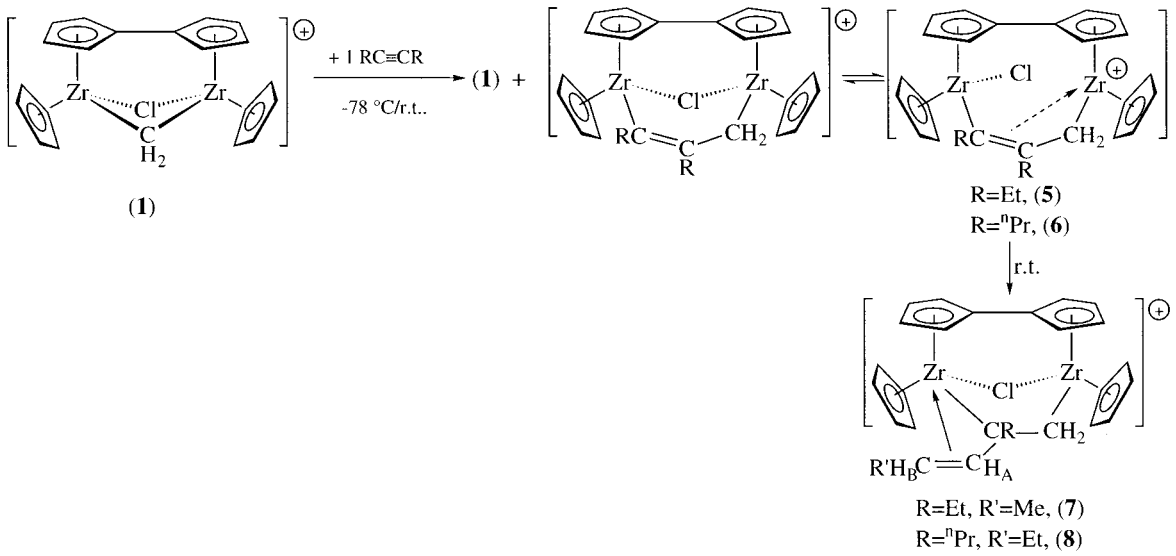
(20) Herrmann, W. A.; Cuenca, T.; Menjón, B.; Herdtweck, E. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 697.

Scheme 3



stretch of 1950 cm^{-1} for C≡C found for compound **2** is slightly low, and the ^{13}C resonances assigned to the acetylenic carbons are slightly deshielding with respect to the normal range for such carbons. The formation of a coordinated allene intermediate known in dimolybdenum chemistry,[21] but not observed in the NMR study as an intermediate species, could not be ruled out.

The species **B2** generated by 2,1-addition of the ^{n}PrC≡CH coordinated alkyne can also achieve a planar "*Zr−CH═CRCD*$_2$" unit, but it does not contain a β-hydrogen and is therefore thermally stable at room temperature. From the NMR data described above, the bonding between the bridging allyl group and the two metal centers in complexes **3** and **4** may be better described as η^1-coordination to one zirconium and η^3 to the other, represented as **B3** in Scheme 2, achieved through nucleophilic attack of the π-orbital C═C bond on the electrophilic Zr(1) center with simultaneous Zr(1)−C(sp^3) bond breaking. The formation of metallocene allyl cationic complexes as deactivated species has been observed in the course of the metalllocene-catalyzed olefin polymerizations.[22] Alkyne C−H bond activation to give the cationic methyl-acetylide $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(CH_3)(C{\equiv}CR)(\mu\text{-}Cl)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]^+$ species, normally observed in the reaction of titanium vinylidene intermediates with various RC≡CH[15] alkynes, was not detected.

Insertion of Internal Alkynes. The results observed in the reactions with terminal acetylenes moved us to extend our study to reactions of cationic complex **1** with analogous internal alkynes. When compound **1** was treated with 1 equiv of RC≡CR (R = Et, ^{n}Pr) in dichloromethane at low temperature (−78 °C) and the reaction mixture warmed to room temperature, the solution slowly changed to afford the moisture-sensitive species $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}Cl)\{\mu\text{-}CH_2C(Et){=}C(Et)\}(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ (**5**) and $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}Cl)\{\mu\text{-}CH_2C(^{n}Pr){=}C(^{n}Pr)\}(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ (**6**), respectively, in ca. 60% yield (Scheme 3).

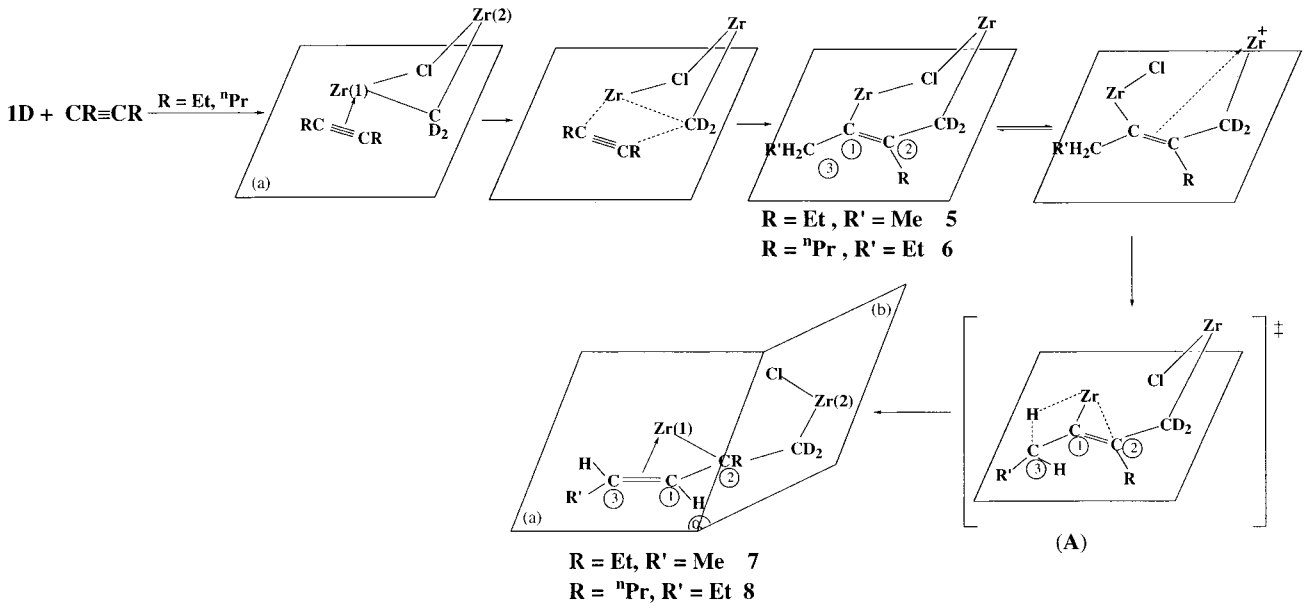
The final products obtained in these reactions always contained a small amount (10% by NMR spectroscopy in CD_2Cl_2) of unreacted compound **1**, and all the efforts made to modify the temperature and the reaction times gave the same results. Isolation of analytically pure samples of **5** and **6** was unsuccessful since their solubility was very similar to that of **1**. Complexes **5** and **6** are not stable in CD_2Cl_2 solutions, and after short times (2−6 h) at room temperature they evolved into the new dinuclear cationic zirconium derivatives $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}Cl)\{\mu\text{-}CH_2C(Et)CH{=}CHMe\}(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ $[BMe(C_6F_5)_3]$ (**7**) and $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}Cl)\{\mu\text{-}CH_2C(^{n}Pr)CH{=}CHEt\}(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ (**8**), respectively. These are not stable in solution for long periods and continue to evolve to an unresolvable mixture of substances.

We have not been able to characterize complexes **5**−**8** by elemental analysis, but all of the NMR spectroscopic data in CD_2Cl_2 are consistent with the structures shown in Scheme 3. The ^1H NMR (CD_2Cl_2) spectra of these compounds show two ABCD spin systems for the fulvalene ligands and two signals due to the cyclopentadienyl ring protons (10 fulvalene and two cyclopentadienyl signals in the $^{13}C\{^1H\}$ NMR spectra).

In the ^1H NMR spectra the most notable resonances are due to the diastereotopic CH_2 hydrogens, which appear as an AB spin system at high-intensity fields (δ_{av} 0.80 ($^2J_{HH}$ = 13.5 Hz) for compound **5** and at δ_{av} 0.41 ($^2J_{HH}$ = 13.1 Hz) for compound **6**), clearly shielding with respect to those observed for the bridging methylene protons in compound **1** (δ_{av} = 7.45, $^2J_{HH}$ = 8.5 Hz.) ($\Delta\delta_{av}$ = 6.65 and 7.04 ppm, respectively) and for the reported $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_2)(\mu\text{-}CH_3)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ complex (δ_{av} = 7.21, $^2J_{HH}$ = 8.25 Hz.).[3] In contrast, the AB spin systems for Zr−CH_2 protons are observed at δ_{av} = 2.97 ($^2J_{HH}$ = 7.0 Hz) and δ_{av} = 2.99 ($^2J_{HH}$ = 6.75 Hz) for **7** and **8**, respectively, deshielded with respect to the corresponding signals in compounds **5** and **6**, but with chemical shifts and coupling constants similar to those observed for complex **2**. Furthermore, the ^1H NMR spectra of **5** and **6** exhibit a pronounced difference in the chemical shifts for the AB protons with high shielding of one of the signals (δ

(21) Froom, S. F. T.; Green, M.; Mercer, R. J.; Nagle, K. R.; Orpen, A. G.; Rodrigues, R. A. *J. Chem. Soc., Dalton Trans.* **1991**, 3171.
(22) Lieber, S.; Prosenc, M. H.; Brintzinger, H. H. *Organometallics* **2000**, *19*, 377, and references therein.

Scheme 4



Planes (a) and (b) symbolize the bent metallocene wedges for Zr(1) and Zr(2) respectively; α denotes the angle between both planes

= −2.16 (**5**) and −2.84 (**6**); $\Delta\delta$ = 5.12 (**5**) and 6.07 (**6**) ppm), suggesting a π interaction between the olefin and the electrophilic zirconium cationic center, with chlorine in a terminal disposition (Scheme 3). Similar NMR behavior has been described as metal-bound methylene protons in η^4-conjugated diene mononuclear zirconocene complexes in metalacyclic systems.[23]

The ^{1}H NMR spectra of compounds **5** and **6** also indicate the presence of two ABK_3 and two $ABCDK_3$ spin systems, respectively, for the alkyl substituents, whereas the ^{1}H NMR spectrum of complex **7** shows one signal (doublet, δ 1.76) for the methyl protons and one ABC_3 spin system for the ethyl group. ABK_3 and $ABCDK_3$ spin systems for the ethyl and propyl groups are observed in the ^{1}H NMR spectrum of **8**. In addition, the ^{1}H NMR spectra show one doublet and one doublet of quartets at δ 3.92 and 3.37 (^3J = 13.5 Hz; ^3J = 6.3 Hz) for complex **7** and one doublet and one doublet of doublets of doublets at δ 3.85 and 3.23 (^3J = 13.5 Hz) for complex **8**, characteristic resonances for a *trans*-H_AC=CH_BR terminal group η^2-coordinated to the zirconium atom. Three carbon resonances at δ 79.3, 149.0, and 173.3 for the Zr−CH_2−CR=CR−Zr moiety and signals for two different alkyl ^{n}Pr substituents are also observed in the ^{13}C{^{1}H} NMR spectrum of complex **6**. The CH_2 carbon resonance (δ 79.3) is found ca. 40 ppm deshielding with respect to the corresponding signal in compound **2**. Analogous chemical shifts have been found for dinuclear derivatives containing bridging alkenyl ligands.[14] All of these spectrocopic data are in agreement with the presence of two nonequivalent chiral metal centers in the complexes **5**−**8**, with only one of the diastereoisomers observed in the solution.

The formation of complexes **5** and **6** can be rationalized using the same reaction pathway described for reactions with terminal acetylenes. When the bulkiness of the alkyne substituent allows its coordination to one of the zirconium centers (R = Et, ^{n}Pr) of the methylene-bridged complex **1** or/and **1D**, insertion into the "*Zr*−*CH*$_2$" bond takes place by an addition mechanism to give compounds **5** and **6**, which contain the bridging "*Zr*−*CR*=*CR*−*CH*$_2$−*Zr*" unit represented in Scheme 4. The rearrangement process of **5** and **6** involves a hydrogen shift from the C3 (of the ethyl or *n*-propyl fragment) to the C1 carbon atom of the bridging alkenyl unit and results in the formation of the new dinuclear cationic zirconium derivatives **7** and **8** (Scheme 4).

Compounds **5** and **6** are stable at room temperature for short periods, although the C(3) substituent possesses β-hydrogens (transition state **A**) which can be involved in a β-elimination process. This could be responsible for the further isomerization, which takes place at room temperature by β−α migration with simultaneous nucleophilic attack of the C2 carbon atom on the electrophilic zirconium center, giving compounds **7** and **8**. Evidence for β-H transfer to metal centers and direct β-H transfer to coordinated olefins has been obtained from studies on olefin polymerizations as potential pathways in catalyst deactivation reactions.[4h,24] Species **7** and **8** are not stable in solution, probably due to the presence of β-hydrogen atoms in their structures, and after 4−6 h the ^{1}H NMR spectra show new signals for unidentified substances.

The faster rearrangement of **5** compared with **6** must be due to the less bulky ethyl substituent. When compound **1** was treated with the acetylenes RC≡CR′ (R = R′ = $SiMe_3$, Ph; R = Me, R′ = $SiMe_3$), under the conditions described above, the starting compound was recovered without modification, probably because the bulkiness of these acetylenes prevents its coordination to the metal center, whereas addition of MeC≡CMe to a solution of **1** in dichloromethane gave a spectroscopically unresolvable mixture of compounds, none of which could be isolated as a pure sample. This result is expected if the reaction pathway already discussed is

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(24) Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Polymer* **1989**, *30*, 428.

followed, since in this case one of the zirconium atoms has β-hydrogens available from a methyl group bound to the vinylic carbon, allowing additional β-elimination processes.

Concluding Remarks

We can conclude that the fulvalene ligand is a very convenient system to link two zirconium atoms, and it provides a valuable strategy to design new types of cationic dinuclear zirconium derivatives and to study their chemical and structural behavior. We have studied the reactivity of the methylene group bridging two zirconium centers in the dinuclear cationic compound $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$, **1**. The reaction with acetylenes affords new types of dinuclear zirconium cationic species, through insertion processes, the nature of the final products depending on the electronic and steric factors of the substituents. Thus, while **1** reacts with $Me_3SiC{\equiv}CH$ to give the hydrido-alkyl species $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}Cl)(\mu\text{-}H)(CH_2C{\equiv}CSiMe_3)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ (**2**), treatment of **1** with internal alkynes $RC{\equiv}CH$ (R = Pr, ^{t}Bu) yields the $\mu\text{-}\eta^1\text{-}\eta^3$-(2-alkyl)allyl compounds $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}Cl)\{\mu\text{-}\eta^1\text{-}\eta^3\text{-}CHC(R){=}CH_2\}(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$, **3** and **4**. The reaction of **1** with internal alkynes $RC{\equiv}CR$ (R = Et, ^{n}Pr) led to the corresponding allyl-vinyl-bridged compounds $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}Cl)\{\mu\text{-}CH_2C(R){=}C(R)\}(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$, **5** and **6**. The presence of β-hydrogen favors the C3−C1 hydrogen shift process in the "μ-$CH_2C(R){=}C(R)$" ligand to give the corresponding dinuclear cationic zirconium derivatives **7** and **8** as observed by NMR spectroscopy.

Experimental Section

General Considerations. All manipulations were performed under argon using Schlenk and high-vacuum line techniques or a glovebox, model HE-63 or VAC HE-543-6. Solvents were purified by distillation under argon from an appropriate drying agent (sodium for toluene, sodium−potassium alloy for hexane, and P_2O_5 for dichloromethane). $Me_3SiC{\equiv}CH$, $^nPrC{\equiv}CH$, $^tBuC{\equiv}CH$, 3-hexyne, and 4-octyne (Aldrich) were commercially obtained and used without further purification. $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$[3b] was prepared by the described procedure. C, H, and N microanalyses were performed on a Perkin-Elmer 240B and/or Heraeus CHN-O-Rapid microanalyzer. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer using KBr pellets. NMR spectra were recorded on a Varian Unity 500 Plus spectrometer, and chemical shifts are referenced to TMS via residual protons (^{1}H) or the carbon resonances (^{13}C) of the solvent.

Synthesis of $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}Cl)(\mu\text{-}H)(CH_2C{\equiv}CSiMe_3)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ (2). Trimethylsilylacetylene (4.2×10^{-2} mL, 0.29 mmol) was added via syringe to a solution of $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ (0.30 g, 0.29 mmol) in dichloromethane (10 mL) at −78 °C. The reaction mixture was warmed to 0 °C and stirred for 30 min. The solvent was removed at this temperature, and **2** was obtained as a yellow oil. Recrystallization from dichloromethane/*n*-hexane gave 0.27 g (84%) of **2**·1/2CH_2Cl_2 as a yellow crystalline solid dichloromethane solvate. IR (KBr): ν (cm^{-1}) 247, 367, 346 (Zr−Cp, Zr−Cl−Zr) 1150 (Zr−H−Zr), 1950 (C≡C). ^{1}H NMR (500 MHz, CD_2Cl_2, 223 K): δ 5.81, 6.72 (s, C_5H_5, 2 × 5H); 4.53, 5.29, 5.56, 6.23, 6.33, 6.71, 6.74, 6.94 (two ABCD spin systems $C_{10}H_8$); 2.97, 2.44 (^2J = 9.9 Hz, ^3J = 1.5 Hz) $CH_2C{\equiv}CSiMe_3$; 0.47 $SiMe_3$; 0.50 (br) *Me*B; −4.67 (^3J = 1.5 Hz) Zr−H−Zr. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 223 K): δ 115.8, 107.5 (C_5H_5); 95.3, 97.8, 101.8, 102.4 109.5, 112.7, 113.6, 116.7 ($C_{10}H_8$); 117.6, 112.3 (C_{ipso}); 104.2, 115.2 ($CH_2C{\equiv}CSiMe_3$); 37.2 ($CH_2C{\equiv}CSiMe_3$), 0.6 ($SiMe_3$); ≈10 (br) *Me*BAr_3. Anal. Calcd for $C_{45}H_{33}BClF_{15}SiZr_2{\cdot}0.5CH_2Cl_2$: C 47.21, H 2.93. Found: C 47.13, H 3.02.

Synthesis of $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}Cl)\{\mu\text{-}\eta^1{:}\eta^3\text{-}CHC(^nPr)CH_2\}(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ (3). 1-Pentyne (0.034 mL, 0.34 mmol) was added via syringe to a solution of $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ (0.35 g, 0.34 mmol) in dichloromethane (10 mL) at −78 °C. The reaction mixture was stirred overnight and then warmed to room temperature and stirred for 30 min. The solvent was removed, and **3** was obtained as an orange solid. Recrystallization from dichloromethane/*n*-hexane gave 0.28 g (75%) of **3**·1CH_2Cl_2 as an orange crystalline solid dichloromethane solvate. IR (KBr): ν (cm^{-1}) 1490 (C=C). ^{1}H NMR (500 MHz, CD_2Cl_2, 203 K): δ 5.84, 6.53 (s, C_5H_5, 2 × 5H); 5.44, 5.55, 5.65, 5.71, 5.97, 6.48, 6.62, 6.74 (two ABCD spin systems, $C_{10}H_8$); 6.90 (d, ^4J = 3.5 Hz, $CH{-}CRCH_2$); 3.20 (d, ^2J = 2.4 Hz), 2.90 (dd, ^2J = 2.4 Hz, ^4J = 3.5 Hz) ($CH{-}CRCH_2$); 2.47, 1.91 (m, $CH_2CH_2CH_3$); 1.59, 1.68 (m, $CH_2CH_2CH_3$); 0.99 (t, $CH_2CH_2CH_3$); 0.50 (br) *Me*B. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 203 K): δ 114.8, 107.4 (C_5H_5); 96.8, 107.6, 108.5, 108.5, 110.4, 113.4, 114.4 120.6 ($C_{10}H_8$); 104.7, 117.3 (C_{ipso}); 164.8 (μ-$CHCR{=}CH_2$); 154.4 (^1J = 111.6 Hz, μ-$CH{-}CR{=}CH_2$); 62.9 (^1J = 147.1 Hz, μ-$CH{-}CR{=}CH_2$); 49.3, 26.3, 14.3 (C_3H_7); ≈10 (br) *Me*BAr_3. Anal. Calcd for $C_{45}H_{31}BClF_{15}Zr_2{\cdot}1CH_2Cl_2$: C 47.21, H 2.84. Found: C 47.49, H 3.20.

Synthesis of $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}Cl)\{\mu\text{-}\eta^1{:}\eta^3\text{-}CHC(^tBu)CH_2\}(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ (4). An analogous procedure described to prepare **3**, using 0.30 g (0.29 mmol) of $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ and 0.037 mL (0.29 mmol) of *tert*-butylacetylene, afforded compound **4**·1CH_2Cl_2 (0.23 g, 71%) as an orange crystalline solid dichloromethane solvate. IR (KBr): ν (cm^{-1}) 1500 (C=C). ^{1}H NMR (500 MHz, CD_2Cl_2, 203 K): δ 5.86, 6.52 (s, C_5H_5, 2 × 5H); 5.47, 5.57, 5.64, 5.65, 6.01, 6.40, 6.57, 6.67 (two ABCD spin systems, $C_{10}H_8$); 6.97 (d, ^4J = 3.9 Hz) (CH-$CRCH_2$); 3.17 (d, ^2J = 5.0 Hz), 3.00 (dd, ^2J = 5.0 Hz, ^4J = 3.9 Hz) ($CH{-}CRCH_2$); 1.24 (*tert*-Bu); 0.50 (br) *Me*B. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 203 K): δ 116.1, 108.3 (C_5H_5); 98.7, 109.5, 110.0, 110.8, 112.4, 115.1, 115.2, 122.9 ($C_{10}H_8$); 102.0, 119.4 (C_{ipso}); 182.7 (μ-$CH{-}CR{=}CH_2$); 146.4 (μ-$CH{-}CR{=}CH_2$); 42.4 (μ-$CH{-}CR{=}CH_2$); 40.4, 31.6 (*tert*-Bu); ≈10 (br) *Me*BAr_3. Anal. Calcd for $C_{46}H_{33}BClF_{15}Zr_2{\cdot}1CH_2Cl_2$: C 47.66, H 2.98. Found: C 47.54, H 3.13.

Synthesis of $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}Cl)\{\mu\text{-}CH_2C(Et){=}C(Et)\}(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ (5). 3-Hexyne (0.050 mL, 0.34 mmol) was added via syringe to a solution of $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ (0.35 g, 0.34 mmol) in dichloromethane (10 mL) at −78 °C. The reaction mixture was stirred overnight and then warmed to room temperature and stirred for 30 min. The solvent was removed, and **5** was obtained as a red-purple solid. Recrystallization from dichloromethane/*n*-hexane gave 0.25 g (64%) of **5**. The isolated red-purple solid consisted mainly of **5**, but it contained an amount of **1** that could not be removed. This prevented us from obtaining correct elemental analysis, although satisfactory spectroscopy data were obtained. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 6.22, 6.51 (s, C_5H_5, 2 × 5H); 5.71, 5.73, 5.78, 6.04, 6.34, 6.68, 6.83, 6.85 (two ABCD spin systems, $C_{10}H_8$); 2.15−2.22 (m, 2H), 1.68−1.74 (m, 2H), 1.10 (t, 3H, ^3J = 7.0 Hz.), 0.91 (t, 3H, ^3J = 7.5 Hz.) ($-CH_2CH_3$); 2.96 (d, 1H, ^2J = 13.5 Hz), −2.16 (d, 1H, ^2J = 13.5 Hz) ($Zr{-}CH_2$); 0.53 (br, *Me*B). The fast rearrangement of **5** in solution (2 h) to **7** prevented us from obtaining a satisfactory $^{13}C\{^1H\}$ NMR spectrum of this substance.

Synthesis of $[\{Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}Cl)\{\mu\text{-}CH_2C(^nPr){=}C(^nPr)\}(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ (6). 4-Octyne (0.034 mL, 0.29 mmol) was added via syringe to a solution of $[\{Zr(\eta^5$-

$C_5H_5)\}_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][BMe(C_6F_5)_3]$ (0.30 g, 0.29 mmol) in dichloromethane (10 mL) at −78 °C. The reaction mixture was stirred overnight and then warmed to room temperature and stirred for 30 min. The solvent was removed, and **6** was obtained as a red-brown solid. Recrystallization from dichloromethane/*n*-hexane gave 0.19 g (59%) of **6**. The isolated red-brown solid consisted mainly of **6**, but it contained an amount of **1** that could not be removed. This prevented us from obtaining correct elemental analysis, although satisfactory spectroscopy data were obtained. ^{1}H NMR (500 MHz, CD_2Cl_2, 195 K): δ 6.23, 6.53 (s, C_5H_5, 2 × 5H); 5.70, 5.74, 5.78, 6.07, 6.28, 6.71, 6.76, 6.89 (two ABCD spin systems, $C_{10}H_8$); 2.00−2.10 (m, 2H), 1.10−1.60 (3m, 3 × 2H), 1.05 (t, 3H, ^3J = 7.0 Hz.), 0.90 (t, 3H, ^3J = 7.5 Hz.) ($-CH_2CH_2CH_3$); 3.25 (d, 1H, ^2J = 13.1 Hz), −2.84 (d, 1H, ^2J = 13.1 Hz) ($Zr-CH_2$); 0.53 (br) MeB. $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 233 K): δ 116.1, 112.4 (C_5H_5); 102.6, 108.5, 110.9, 111.1, 111.8, 111.9, 112.5, 116.4, 118.1, 122.9 ($C_{10}H_8$); 173.3 ($Zr-CR{=}C$); 149.0 ($=CR-CH_2-Zr$); 41.9, 31.4, 23.4, 24.9 ($=C-(CH_2)_2-CH_3$); 15.0, 15.9 ($=C-(CH_2)_2-CH_3$); 79.3 ($Zr-CH_2$); ≈ 10 (br) $MeBAr_3$.

Synthesis of [{Zr(η^5-C_5H_5)}$_2$(μ-Cl){μ-CH_2C(Et)CH=CHMe}(μ-η^5-C_5H_4-η^5-C_5H_4)] [BMe(C_6F_5)$_3$] (7). Red-purple solutions of **5** in CD_2Cl_2 converted to **7** (>95%) after 2 h. The formation of **7** was monitored by ^{1}H NMR spectroscopy. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 6.22, 6.23 (s, C_5H_5, 2 × 5H); 5.65−6.90 (two ABCD spin systems, $C_{10}H_8$); 3.92 (d, *H*C=CHMe, 1H, ^3J = 13.5 Hz); 3.37 (dq, HC=C*H*Me, 1H, ^3J = 13.5 Hz, ^3J = 6.3 Hz); 1.76 (d, HC=CH*Me*, 3H, ^3J = 6.3 Hz); 3.27, 2.67 (d, 2 × 1H, ^2J = 7.0 Hz) ($Zr-CH_2$); 2.30−2.10 (2H), 1.00 (3H, C=CH−C*Et*); 0.50 (br) MeB. The fast decomposition of **7** in solution (4 h) prevented us from obtaining a satisfactory $^{13}C\{^1H\}$ NMR spectrum of this substance.

Synthesis of [{Zr(η^5-C_5H_5)}$_2$(μ-Cl){μ-CH_2C(^{n}Pr)CH=CHEt}(μ-η^5-C_5H_4-η^5-C_5H_4)] [BMe(C_6F_5)$_3$] (8). Red-purple solutions of **6** in CD_2Cl_2 converted to **8** (>95%) after 6 h. The formation of **8** was monitored by ^{1}H NMR spectroscopy. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 6.22, 6.24 (s, C_5H_5, 2 × 5H); 5.60−6−95 (two ABCD spin systems, $C_{10}H_8$); 3.85 (d, *H*C=CHEt, 1H, ^3J = 13.5 Hz); 3.23 (ddd, HC=C*H*Et, 1H, ^3J = 13.5 Hz); 3.30, 2.69 (d, 2 × 1H, ^2J = 6.75 Hz) ($Zr-CH_2$); 2.50−0.80 (ABK_3 spin system HC=CH*Et* and $ABCDK_3$ spin system HC=CH^n*Pr*); 0.50 (br) MeB. The fast decomposition of **8** in solution (6 h) prevented us from obtaining a satisfactory $^{13}C\{^1H\}$ NMR spectrum of this substance.

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