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Article

Dynamic Topochemical Reaction Control—A Principle and Its Application in *ansa*-Metallocene Synthesis[†]

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[‡]X-ray crystal structure analyses.

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The Cp-alkenyl and Cp-dienyl ligand systems **5** and **8** were prepared by fulvene routes. Subsequent transmetalation gave the respective (Cp-propenyl)$_2$-, (Cp-butenyl)$_2$-, (Cp-pentadienyl)$_2$-, and (Cp-hexadienyl)$_2$ZrCl$_2$ and -HfCl$_2$ complexes **6**, **9**, and **10**. In the crystal these complexes favor metallocene conformations that feature the alkenyl and dienyl substituents far separated from each other at the open front side of the bent metallocene wedge. Photolysis in the solid state consequently did not result in an intramolecular C−C coupling reaction but led to *E*/*Z* isomerization of the alkenyl units. In solution rapid conformational metallocene equilibration takes place. Photolysis of the (Cp-alkenyl)$_2$ZrCl$_2$ complexes **6** in solution very efficiently resulted in the formation of the cyclobutylene-bridged *ansa*-zirconocene isomers **11** by rapid intramolecular [2 + 2] cycloaddition reaction by means of a dynamic topochemical reaction control. Photolysis of the (Cp-dienyl)$_2$ZrCl$_2$ and -HfCl$_2$ complexes (**9**, **10**) in solution proceeded analogously to efficiently yield the cyclooctadienylene bridged *ansa*-metallocenes (**12**, **13**) by formal dynamic topochemical [4 + 4] cycloaddition reaction control.

Introduction

Chemical reactions in the solid state are determined by the position of the atoms and molecules in the crystal lattice more than anything else because they necessarily have to proceed with a minimum of movement around their fixed positions.[1] This topochemical principle has led to the discovery of a sizable number of remarkable topochemically controlled reactions of mostly organic molecules in single crystals or in the solid state in general.[2,3] Some most noteworthy examples come from the pioneering work by Schmidt et al.[4,5] A typical frequently cited example is the photochemical [2 + 2] cycloaddition reaction of pairs of *trans*-cinnamic acid. This takes place from the crystalline α-phase to form the head-to-tail dimer α-truxillic acid, and upon photolysis of the crystalline β-phase it forms the head-to-head cyclobutane derivative (β-truxillic acid). In both of these crystalline phases the cinnamic acid C═C double bonds are oriented close to each other within 3.6−4.1 Å. Photolysis of the *trans*-cinnamic acid crystalline γ-phase, where the separation is much larger, does not result in C−C bond formation. Photolysis of *trans*-cinnamic acid in solution only results in cis−trans isomerization of the central C═C double bond.

Topochemical reaction control has been achieved in solution. In these examples the reacting C═C double bonds were attached at rigid frameworks in favorable distances and

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[†] Dedicated to Professor Wolfgang Kirmse on the occasion of his 80th birthday.

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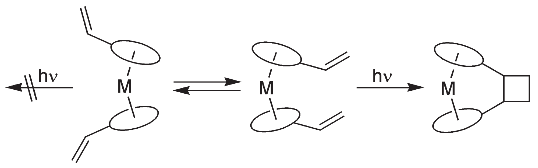
orientation to allow the photochemical formation of the cycloadducts to take place. Notable examples were described by Hopf et al., making use of *p*-cyclophane-derived systems.[6] Even ladderane formation could be achieved in this way.

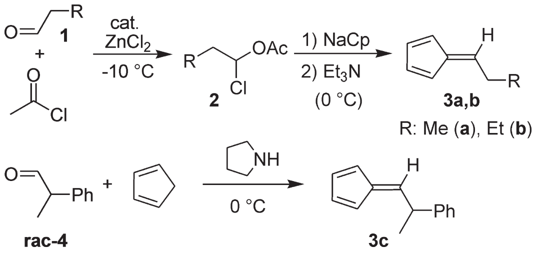
It occurred to us that bent-metallocene frameworks could offer a unique new possibility to set the scene for a different type of topochemical reaction control, namely by bringing the reacting C=C double bonds into a suitable orientation by means of their characteristic conformational features. The bent metallocenes usually undergo rapid rotation around their Cp−metal vectors.[7] Because of the typical bent Cp−M−Cp situation this may bring conjugated alkenyl substituents in a manifold of relative orientations to each other. The global conformational minimum will feature these substituents oriented toward the open front side of the bent metallocene wedge, where their large spatial separation would preclude any coupling reaction to occur. However, there may be cases where local minimum conformations become populated in an equilibrium situation that bring the alkenyl substituent C=C bonds close to each other in a favorable arrangement for a photochemical cycloaddition to take place. Indeed, we[8] and others[9] had shown that *ansa*-metallocene formation is possible by intramolecular photochemical [2 + 2] cycloaddition of suitably bis-alkenyl-substituted bent-metallocene systems in solution. However, it remained to be shown that these reactions really proceeded by a unique "dynamic topochemical reaction control". Such a control would have become indicated by the observation of a formal reversal of the results of the photolysis of a bis(alkenyl-Cp) bent metallocene in the solid state and in solution relative to the conventional topochemically controlled reaction: in the crystal the unfavorable fixed metallocene conformation would in most cases preclude the intramolecular [2 + 2] cycloaddition from taking place, whereas in solution this would in a variety of cases become possible because of a release of this conformational fixture (see Scheme1).

We here wish to report about a series of examples from (alkenyl-Cp)$_2$- and (butadienyl-Cp)$_2$MCl$_2$ chemistry (M = Zr, Hf) where the use of suitably substituted examples has allowed us to detect just these characteristic differences in photochemical behavior in the solid state and in solution, as would be expected for such a dynamic topochemical reaction control.

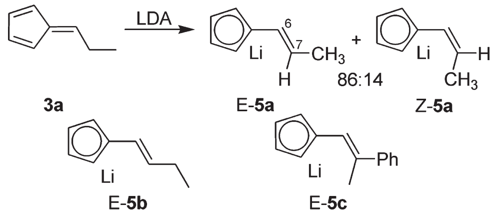
Scheme 1



Scheme 2



Scheme 3



Results and Discussion

Synthesis of the Alkenyl- and Dienyl-Substituted Group 4 Bent-Metallocene Complexes. As we shall see, it was crucial for our analysis to have suitably substituted (alkenyl-Cp)$_2$- and (dienyl-Cp)$_2$MCl$_2$ complexes available. These were prepared by means of fulvene routes. We prepared the fulvenes **3a**,**b** by means of treatment of the respective 1-acetoxy-1-chloroalkane (**2a**,**b**) with sodium cyclopentadienide, followed by triethylamine as described by Neuenschwander et al.[10] The somewhat sensitive fulvenes (**3a**,**b**) were obtained as yellow oils. The fulvene **3c** was prepared by the "Stone/Little procedure"[11] from cyclopentadiene, the aldehyde *rac*-**4**, and pyrrolidine (Scheme 2).[12]

Deprotonation of these fulvenes was effected by treatment with lithium diisopropylamide (LDA) in tetrahydrofuran. The products (**5a**−**c**) were isolated (ca. 70−90% yields) and spectroscopically characterized (Scheme 3).

Deprotonation of **3a** gave a ca. 86:14 mixture of *E*-**5a** and *Z*-**5a**. The isomers were identified by their typical vicinal 6-H/7-H coupling constants of 15.4 Hz (*E*) and 11.2 Hz (*Z*), respectively, and their ^{13}C NMR methyl substituent resonances at δ 18.6 (*E*) and δ 15.5 (*Z*). Deprotonation of **3b** gave mainly a single (1-butenyl-Cp)Li isomer that was identified as the *E*-**5b** product (^{1}H NMR *J*(6-H/7-H) = 15.4 Hz). Similarly, we have obtained a single isomer of **5c**, which we have assigned as *E*-**5c**.

We then reacted the 86:14 mixture of the reagent *E*-**5a** and Z-**5a** with ZrCl$_4$(THF)$_2$ in tetrahydrofuran. Workup gave a

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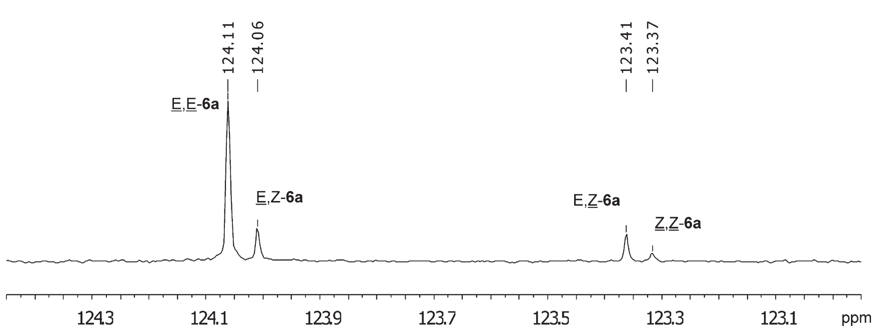
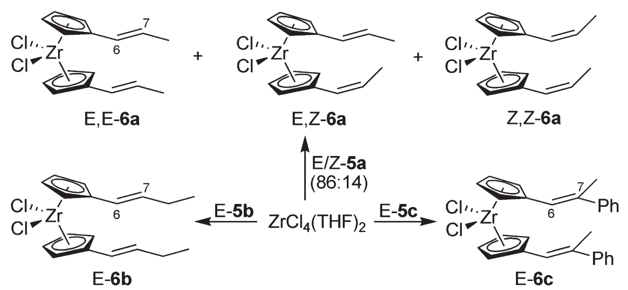
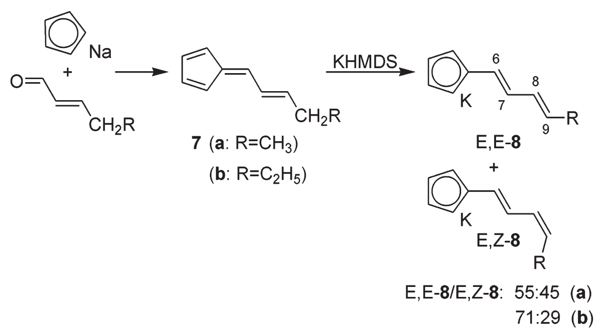


Figure 1. ^{13}C NMR spectrum of the *E*,*E*-, *E*,*Z*-, *Z*,*Z*-**6a** mixture (C6 signals are shown) at 298 K and 125.7 MHz in CD_2Cl_2.

Scheme 4



Scheme 5



mixture of the three products *E*,*E*-**6a**, *E*,*Z*-**6a**, and *Z*,*Z*-**6a** in a ratio of 18:7:1, which was isolated in a combined yield of 53% (Scheme 4). The major component of the mixture was separated and eventually characterized by X-ray diffraction (see below). The ^{1}H/^{13}C NMR signals of the components overlap heavily. The mixture is best characterized by the well-separated C6 ^{13}C NMR signals (see Figure 1). Complex *E*,*E*-**6a** features the C6 resonance of the pair of symmetry-equivalent Cp-(*E*)-CH=CHCH$_3$ ligands at δ 124.11 (in CD_2Cl_2 at room temperature), whereas the *E*,*Z*-**6a** isomer shows a 1:1 intensity pair of the corresponding C6 carbon atoms at δ 124.06 (*E*) and δ 123.41 (*Z*). There remains a single signal at δ 123.37, which we tentatively assign to the pair of Cp-(*Z*)-CH=CHCH$_3$ ligands of the minor *Z*,*Z*-**6a** isomer.

The observed *E*,*E*-**6a**:*E*,*Z*-**6a**:*Z*,*Z*-**6a** ratio corresponds to an overall alkenyl *E*:*Z* ratio of 83:17, which is very close to the *E*:*Z* ratio of the alkenyl side chain in the original reagent *E*-/*Z*-**5a**. The reaction of the ethyl-substituted reagent *E*-**5b** with $ZrCl_4(THF)_2$ was carried out analogously. It gave only a single product, namely *E*,*E*-**6b**, which was isolated in 55% yield. In solution the compound shows a pair of symmetry-equivalent Cp-(*E*)-CH=CHEt ligands; they feature a pair of 6-H (δ 6.22) and 7-H (δ 6.14) ^{1}H NMR resonances with a characteristic vicinal coupling constant of $^3J_{HH}$ = 15.8 Hz. The analogous reaction of the reagent *E*-**5c** with $ZrCl_4(THF)_2$ furnished the metallocene *E*,*E*-**6c** (73% isolated) as a single isomer (^{1}H NMR: δ 6.63 (6-H)).

The Cp-dienyl systems were also prepared by means of fulvene routes. We prepared the new fulvenes **7a** (R = CH$_3$) and **7b** (R = ethyl) in analogy to a procedure developed by Neuenschwander et al.,[13] which used sodium ethoxide as the base to deprotonate cyclopentadiene and react the resulting sodium cyclopentadienide with the corresponding α,β-unsaturated aldehydes in ethanol at −20 °C. The fulvenes **7a**,**b** were both isolated in ca. 30% yield. Their NMR analysis revealed the presence of only *trans*-C7−C8 C=C double bonds in these products (for details see the Supporting Information).

The conjugated fulvenes **7a**,**b** were deprotonated by treatment with potassium hexamethyldisilylamide (KHMDS) in diethyl ether. We isolated a 55:45 mixture of *E*,*E*-**8a** and *E*,*Z*-**8a** in a combined yield of 95%. The NMR analysis (see the Experimental Section and the Supporting Information) revealed the presence of a *trans*-C6−C7 C=C double bond for each of the isomers and a *trans*-C8−C9 linkage (^3J(H8, H9) = 14.2 Hz) for *E*,*E*-**8a** and a *cis*-C8−C9 linkage (^3J(H8, H9) = 10.5 Hz) for the *E*,*Z*-**8a** isomer. The KHMDS deprotonation reaction of the fulvene **7b** gave a similar result. We obtained a 71:29 mixture of the substituted cyclopentadienide products *E*,*E*-**8b** and *E*,*Z*-**8b** isolated in a combined yield of 86% (see Scheme 5).

Transmetalation of the 55:45 mixture of *E*,*E*-**8a** and *E*,*Z*-**8a** with $ZrCl_4(THF)_2$ gave a 4:4:1 mixture of the respective substituted zirconocene dichlorides *E*,*E*;*E*,*E*-**9a**, *E*,*E*;*E*,*Z*-**9a**, and *E*,*Z*;*E*,*Z*-**9a** (combined yield, isolated, 71%). The NMR analysis showed that in each case the C6−C7 C=C double bonds of the conjugated dienyl side chains were in an *E* configuration, whereas the terminal C8−C9 C=C double bonds were responsible for the formation of the isomeric mixture. The overall C8−C9 *E*:*Z* ratio was found to be 67:33 for **9a**, which slightly deviated from the original *E*:*Z* ratio found in the respective reagent **8a**. The reaction of the *E*-/*Z*-**8a** mixture with $HfCl_4(THF)_2$ in THF gave a similar result (4:4:1 ratio of the three isomers of **10a**; see Scheme 6).

Treatment of the 71:29 mixture of the *E*,*E*-**8b**/*E*,*Z*-**8b** reagents with $ZrCl_4(THF)_2$ gave the product **9b** as a 6:4:1 mixture of the three respective isomers (see Scheme 6). This corresponds to an overall C8−C9 *E*:*Z* ratio of 73:27, which in this case is close to that of the starting material. The mixture was isolated in a combined yield of 70%. We also

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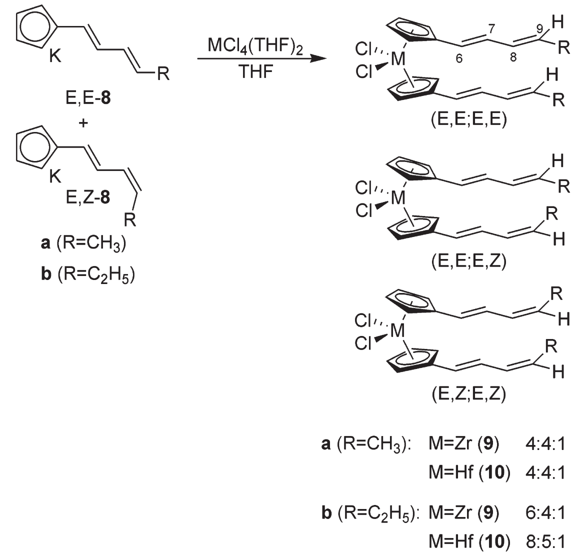
[13] Neuenschwander, M.; Meuche, D.; Schaltegger, H. *Helv. Chim. Acta* **1964**, *47*, 1022–1032.

Scheme 6



prepared the corresponding hafnium compounds (72% yield, 8:5:1 ratio of the *E,E;E,E*-, *E,E;E,Z*-, and *E,Z;E,Z*-**10b** isomers, overall C8−C9 *E*:*Z* ratio 75:25).

Characterization by X-ray Diffraction. Three typical examples of the alkenyl- and dienyl-substituted group 4 bent metallocenes were characterized by X-ray crystal structure analyses. Single crystals of the pure (Cp-(*E*)-CH=CH-CH_3)$_2$ZrCl$_2$ isomer *E,E*-**6a** were obtained from the mixture of isomers by crystallization from a toluene solution at −30 °C. The structure of complex *E,E*-**6a** (see Figure 2) shows a typical bent-metallocene core with a Cl1−Zr−Cl1* angle of 96.31(2)° and a Cp(centroid)−Zr−Cp*(centroid) angle of 129.9°. The metallocene features a C_2-symmetric conformation that has both of the (*E*)-CH=CHCH$_3$ substituents oriented toward the open front side of the bent-metallocene wedge. This results in a large vertical separation of the pair of olefinic π-systems (distances C6$\cdots$C6* = 6.551 Å, C7$\cdots$C7* = 8.080 Å). In addition the alkenyl C=C double bonds are found slightly offset in their projection onto the metallocene σ plane (dihedral angle C7−C6$\cdots$C6*−C7* = 125.7°). The closely related complex *E,E*-**6b** was also characterized by X-ray diffraction. It shows a very similar structure. Both (*E*)-CH=CHC$_2$H$_5$ substituents are found oriented toward the open front side of the metallocene in an overall C_2-symmetric geometry (dihedral angle C7−C6$\cdots$C6*−C7* = −97.0°; for further details and a figure of the structure of complex *E,E*-**6b** in the crystal, see the Supporting Information).

Single crystals of the (Cp-dienyl)$_2$HfCl$_2$ complex *E,E;E,E*-**10b** (R = ethyl) were obtained from a toluene/pentane solvent mixture. To the best of our knowledge, it represents the first crystal structure analysis of a bent-metallocene complex with a butadienyl-derived conjugated Cp side chain. In the crystal the molecule attains a close to C_s-symmetric molecular geometry (see Figure 3). The conjugated side chains exhibit the expected alternation of carbon−carbon single and double bonds. The dienyl chains are in a coplanar orientation with their Cp rings, which allows for optimal overlap of their π-electron systems. The pairs of C=C double bonds in both the dienyl side chains are found in the *E* configuration. It is seen in the respective projection that the system shows a metallocene conformation that has both of the −CH=CHCH=CHC$_2$H$_5$ chains oriented toward the open front side of the metallocene. The C1(Cp)−C6(dienyl) vector is almost perfectly oriented in the bisecting plane of the Cl1−Hf−Cl2 σ unit. Both attached chains then are offset to the Hf−Cl1 side which has both the C6−C7 and the C26−C27 vectors oriented similarly in the projection (see Figure 3). This overall orientation leads to a large vertical separation of the two substituent π systems from each other across the separating metallocene σ-ligand plane.

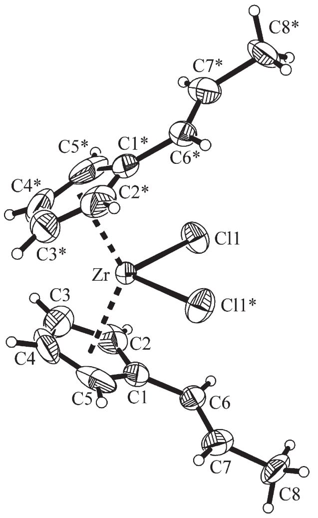


Figure 2. View of the molecular geometry of the metallocene complex *E,E*-**6a**. Selected bond lengths (Å) and angles (deg) (major component): Zr−Cl1 = 2.4376(4), Zr−C$_{Cp}$ = 2.464(2)−2.549(2), C1−C6 = 1.489(3), C6−C7 = 1.313(6), C7−C8 = 1.555(15); Cl1−Zr−Cl1* = 96.31(2), C1−C6−C7 = 122.3(3), C6−C7−C8 = 124.2(6), C1−C6−C7−C8 = 178.3(7). Throughout this paper thermal ellipsoids are depicted at the 50% probability level.

Photolysis of the (Cp-CH=CHR)$_2$ZrCl$_2$ Systems. We performed the photolysis of the 18:7:1 mixture of the *E,E*-, *E,Z*- and *Z,Z*-**6a** isomers in the solid state. For this purpose we precipitated a thin film of **6a** on the glass wall of a Schlenk flask and irradiated it with Pyrex-filtered UV light for ca. 3 h at room temperature. During this time an almost complete cis−trans isomerization took place and we obtained almost pure *E,E*-**6a** (see Figure 4). On redissolution in CD$_2$Cl$_2$ the compound features a pair of symmetry-equivalent Cp-(*E*)-CH=CHCH$_3$ ligands (^{1}H NMR δ 6.25 (dq, $^3J_{H,H}$ = 15.8 Hz, $^4J_{H,H}$ = 1.6 Hz, 6-H), δ 6.10 (dq, $^3J_{H,H}$ = 15.8 Hz, $^3J_{H,H}$ = 6.7 Hz, 7-H)) The corresponding ^{13}C NMR signals were found at δ 124.1 (C6), δ 129.2 (C7) and δ 18.6 (C7-CH$_3$).

Photolysis (HPK 125, Pyrex filter) of the 18:7:1 mixture of *E,E*-, *E,Z*-,and *Z,Z*-**6a** isomers in dichloromethane for 2.5 h at room temperature resulted in a complete conversion to the *ansa*-metallocene isomers Me$_2$-*cis*-**11a** and Me$_2$-*trans*-**11a** in a ratio of 1.7:1. The mixture was isolated on a preparative scale in a combined yield of 72% (see Scheme 7). The same mixture of [2 + 2] photocycloaddition products was obtained by photolyzing the pure *E,E*-**6a** isomer, which was obtained from the solid-state photolysis of the **6a** isomer mixture, on redissolution in CD$_2$Cl$_2$. The major Me$_2$-*cis*-**11a** isomer was characterized by an X-ray crystal structure analysis (see below). This structure and the NMR analysis revealed that the metallocene fragment is 1,2-cis-connected to the newly formed cyclobutane rings in both of the products **11a**. In Me$_2$-*cis*-**11a** the spectra feature an averaged C_s-symmetric compound with the Cp rings and methyl substituents

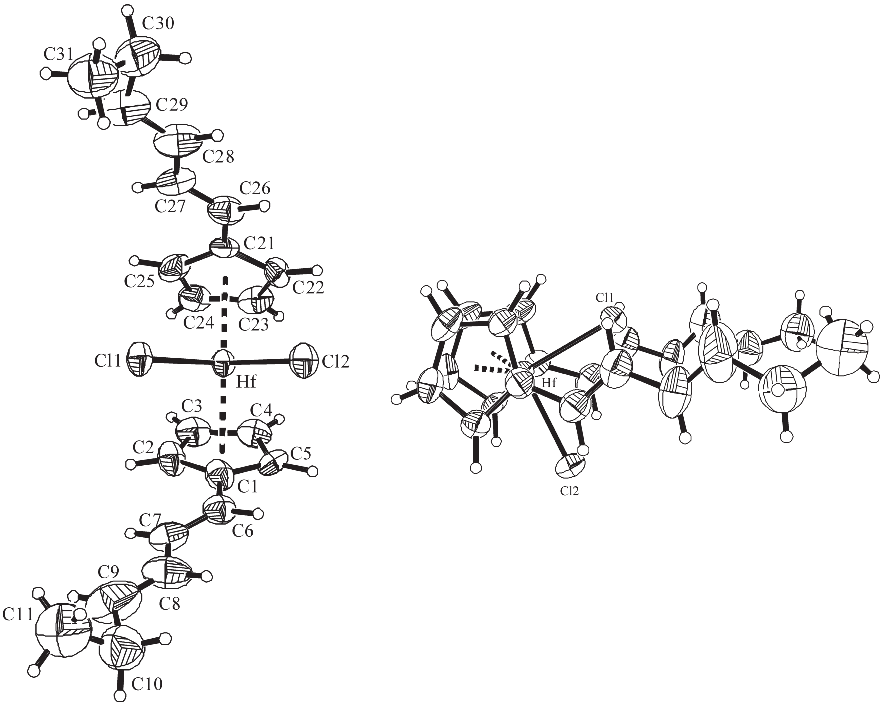


Figure 3. Two projections of the molecular geometry of the hafnium complex *E*,*E*;*E*,*E*-**10b**. Selected bond lengths (Å) and angles (deg) (major components): Hf−Cl1 = 2.411(2), Hf−Cl2 = 2.420(2), Hf−C_{Cp} = 2.447(10)−2.565(19), C1−C6 = 1.47(3), C21−C26 = 1.49(2), C6−C7 = 1.35(2), C26−C27 = 1.34(2), C7−C8 = 1.45(2), C27−C28 = 1.44(2), C8−C9 = 1.33(3), C28−C29 = 1.36(2), C9−C10 = 1.58(2), C29−C30 = 1.58(2), C10−C11 = 1.46(2), C30−C31 = 1.46(2); Cl1−Hf−Cl2 = 96.60(9), C1−C6−C7 = 125(1), C21−C26−C27 = 124(1), C6−C7−C8 = 125(1), C26−C27−C28 = 123(1), C7−C8−C9 = 124(2), C27−C28−C29 = 122(1), C8−C9−C10 = 139(2), C28−C29−C30 = 114(2), C9−C10−C11 = 96(3), C29−C30−C31 = 106(2).

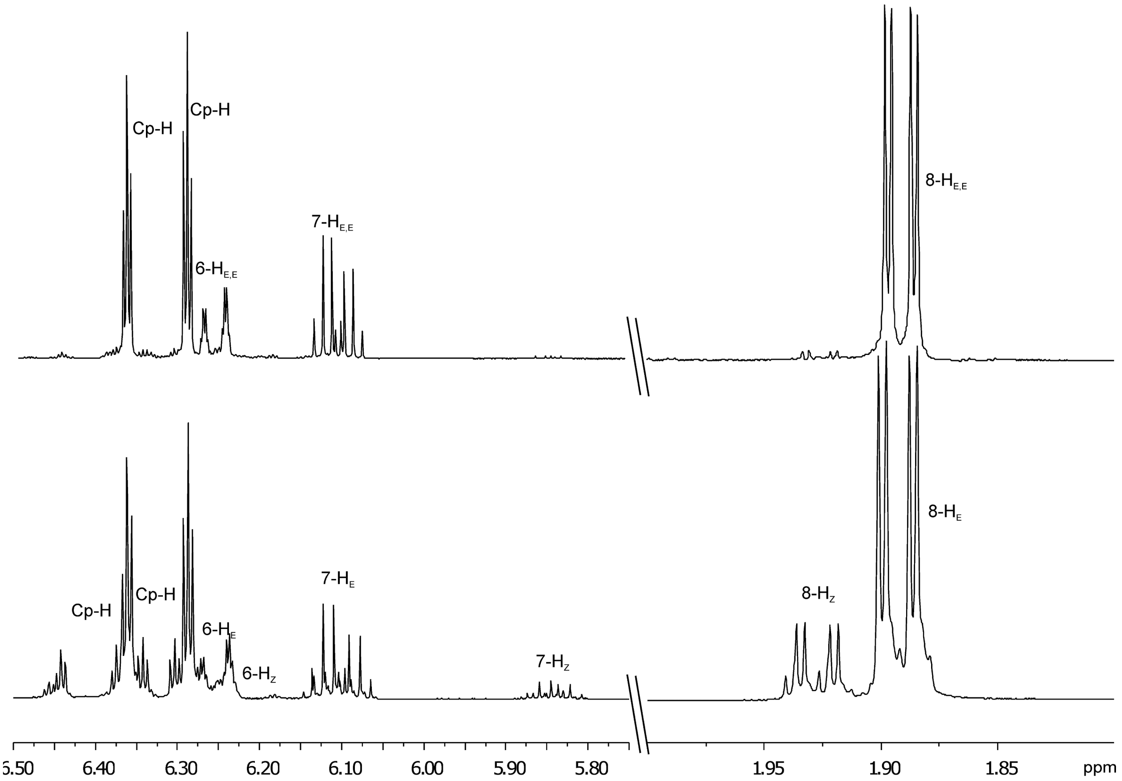
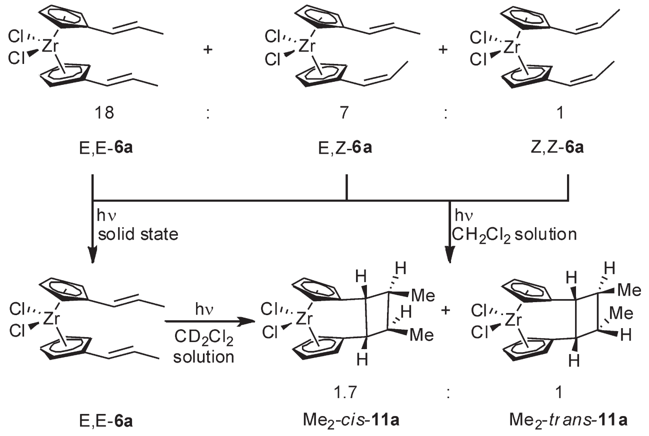


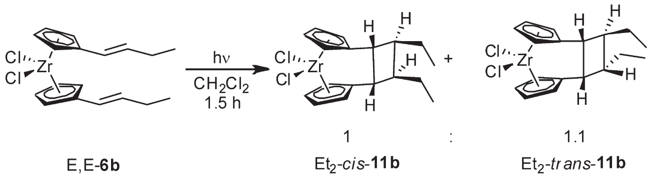
Figure 4. ^{1}H NMR spectrum of the **6a** isomers before (bottom) and after (top) photolysis in the solid state (599.6 MHz, CD_2Cl_2, 298 K).

oriented trans to each other. In the minor Me_2-*trans*-**11a** isomer one Me substituent is oriented trans to Cp and the other cis. The observed 1.7:1 ratio of Me_2-*cis*-**11a** to Me_2-*trans*-**11a** would correspond to an overall 81:19 ratio of

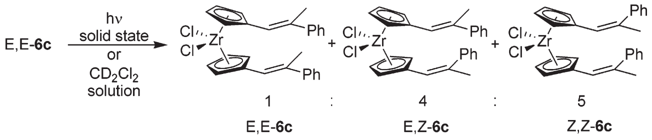
Scheme 7



Scheme 8



Scheme 9



trans- to *cis*-CH=CHCH$_3$ units having been connected. This is close to the *trans*-/*cis*-alkenyl ratio of the original 18:7:1 mixture of the **6a** precursor isomers, but it should be remembered that the 1.7:1 **11a** isomer mixture is also obtained by photolysis of the pure *E*,*E*-**6a** precursor.

The photolysis reaction of the ethyl-substituted (Cp-alkenyl)$_2$ZrCl$_2$ complex **6b** leads to a similar result. UV irradiation of a solution of the pure *E*,*E*-**6b** isomer in CH$_2$Cl$_2$ (1.5 h, room temperature, Pyrex filter) gives the isomeric [2 + 2] cycloaddition products Et$_2$-*cis*-**11b** and Et$_2$-*trans*-**11b** in a 1:1.1 ratio (isolated in 83% yield; see Scheme 8). This corresponds to a hypothetical CpCH=CHEt trans to cis ratio of 74:26. The products were characterized spectroscopically (for details see the Experimental Section and the Supporting Information), and both were characterized by X-ray diffraction (see below).

Photolysis of the highly substituted complex *E*,*E*-**6c** marked the limits of [2 + 2] cyclobutylene-bridged *ansa*-metallocene formation. As expected, the UV irradiation of complex *E*,*E*-**6c** in the solid state only resulted in *E*/*Z* isomerization of the trisubstituted double bonds, resulting in the rapid formation of a mixture of the nonbridged *E*,*E*-**6c**, *E*,*Z*-**6c**, and *Z*,*Z*-**6c** metallocene isomers in a 1:4:5 ratio (see Scheme 9). Photolysis of the pure *E*,*E*-**6c** isomer in CD$_2$Cl$_2$ solution in this case did not result in any measurable formation of intramolecular [2 + 2] cycloaddition products. Instead, we observed a rapid *E*/*Z* double-bond isomerization to take place to yield the same 1:4:5 mixture of the (Cp-alkenyl)$_2$ZrCl$_2$ isomers of **6c**.

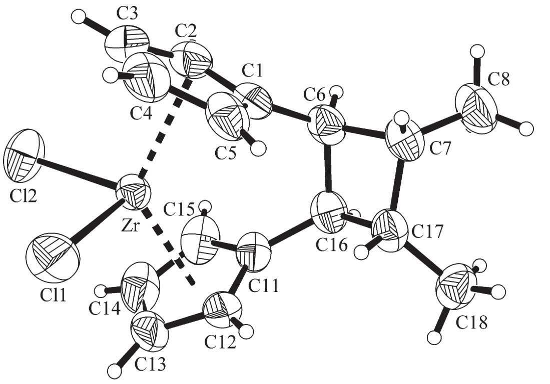


Figure 5. View of the molecular structure of the *cis*-dimethylcyclobutylene-bridged *ansa*-zirconocene complex Me$_2$-*cis*-**11a**. Selected bond lengths (Å) and angles (deg): Zr−Cl1 = 2.437(1), Zr−Cl2 = 2.435(1), Zr−C$_{\mathrm{Cp}}$ = 2.477(4)−2.521(3), C1−C6 = 1.498(5), C11−C16 = 1.502(5), C6−C7 = 1.568(5), C16−C17 = 1.545(5), C7−C8 = 1.501(5), C17−C18 = 1.519(5), C6−C16 = 1.571(5), C7−C17 = 1.551(7); Cl1−Zr−Cl2 = 97.77(4), C1−C6−C7 = 116.5(3), C11−C16−C17 = 119.4(3), C6−C7−C8 = 113.0(3), C16−C17−C18 = 116.7(3), C1−C6−C16 = 113.7(3), C11−C16−C6 = 115.5(3), C6−C7−C17 = 89.7(3), C16−C17−C7 = 89.1(3), C6−C16−C17 = 89.7(3), C16−C6−C7 = 87.6(3).

Structural Characterization of the Substituted Cyclobutylene-bridged *ansa*-Zirconocene Complexes. Single crystals of the Me$_2$-*cis*-**11a** *ansa*-metallocene (see Figure 5) were grown by slow cooling of a toluene solution of the Me$_2$-*cis*-/Me$_2$-*trans*-**11a** mixture of isomers. The compound shows an *ansa*-metallocene framework characterized by a Cp(centroid)−Zr−Cp(centroid) angle of 126.2° and a Cl1−Zr−Cl2 σ-ligand angle of 97.77(4)° (see Figure 5). The Zr−C(Cp) distances are in the range 2.477(4)−2.521(3) Å. The four-membered carbocycle that was formed by [2 + 2] photocycloaddition of the former alkenyl substituents at the Cp rings is oriented toward the narrow back side of the bent-metallocene wedge. The Cp rings are connected cis to each other at the bridging atoms C6 and C16. The methyl substituents at the distal cyclobutane C7−C17 bond are found to be oriented cis to each other. The four-membered carbocycle in Me$_2$-*cis*-**11a** is slightly puckered (dihedral angle C7−C6−C16−C17 = 14.8(2)°).[14]

Upon cooling of the 1:1.1 mixture of the Et$_2$-*cis*-**11b**/Et$_2$-*trans*-**11b** isomers in toluene/pentane we obtained single crystals that contained these two complexes in a 2:1 ratio (see Figure 6). The quality of the data set and the structure solution was not sufficient to allow for a detailed discussion of the specific structural data of this pair of complexes. It served, however, to support the general structural assignments of these compounds as the Et$_2$-*cis*- and Et$_2$-*trans*-**11b** isomers.

Photolysis of the (Cp-dienyl)$_2$MCl$_2$ Complexes. Photolysis of the 4:4:1 mixture of the (Cp-pentadienyl)$_2$ZrCl$_2$ isomers *E*,*E*;*E*,*E*-**9a**, *E*,*E*;*E*,*Z*-**9a**, and *E*,*Z*;*E*,*Z*-**9a** was carried out in solution and in the solid state (see Scheme 10). Irradiation of the mixture as a polycrystalline film resulted in an effective cis/trans isomerization of the distal C=C double bond of the conjugated dienyl system to eventually yield the pure *E*,*E*;*E*,*E*-**9a** metallocene isomer. Its ^{1}H NMR spectrum features the 7-H resonance at δ 6.34 and the corresponding 6-H signal

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[14] Eliel, E. L.; Wilen, S. H.; Doyle, M. P. *Basic Organic Stereochemistry*; Wiley-Interscience: New York, 2001.

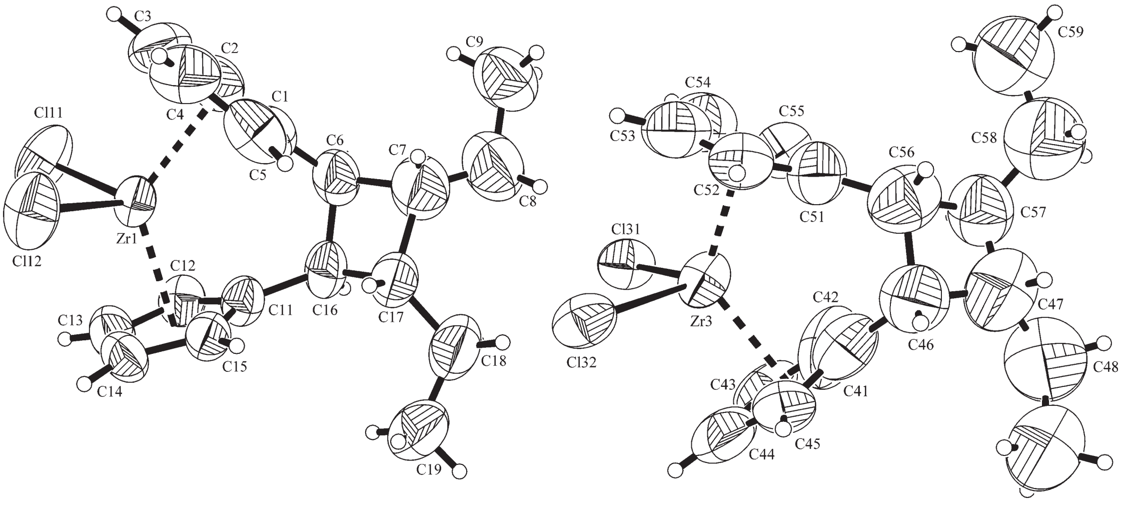
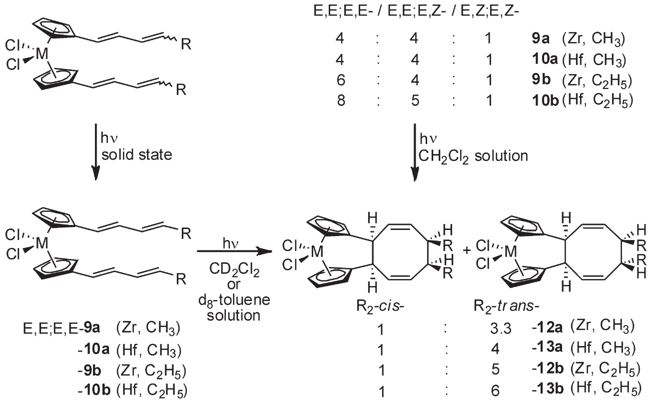


Figure 6. Projections of the molecular structures of the Et_2-*cis*-**11b** (left) and Et_2-*trans*-**11b** (right) isomers.

Scheme 10



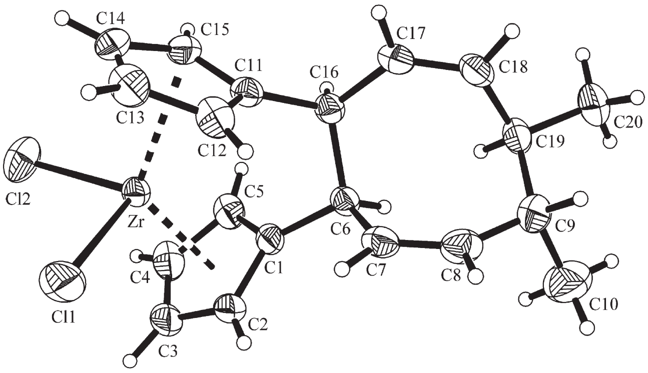


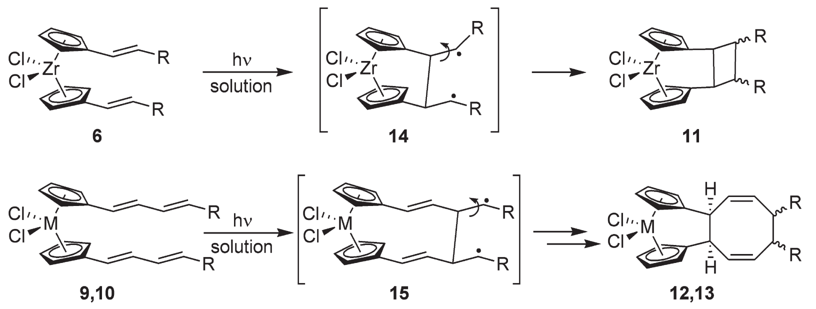
Figure 7. View of the molecular structure of the cyclooctadienylene-bridged *ansa*-zirconocene complex Me_2-*trans*-**12a**. Selected bond lengths (Å) and angles (deg): Zr−Cl1 = 2.442(1), Zr−Cl2 = 2.439(1), Zr−C_{Cp} = 2.470(2)−2.527(2), C1−C6 = 1.515(3), C11−C16 = 1.515(3), C6−C7 = 1.505(3), C16−C17 = 1.516(3), C7−C8 = 1.323(3), C17−C18 = 1.322(3), C8−C9 = 1.505(4), C18−C19 = 1.502(3), C9−C10 = 1.521(4), C19−C20 = 1.535(3), C6−C16 = 1.567(3), C9−C19 = 1.549(3); Cl1−Zr−Cl2 = 97.87(3), C1−C6−C7 = 113.4(2), C11−C16−C17 = 110.2(2), C6−C7−C8 = 127.3(2), C16−C17−C18 = 128.1(2), C1−C6−C16 = 108.3(2), C11−C16−C6 = 110.3(2), C6−C16−C17 = 115.2(2), C16−C6−C7 = 113.2(2), C7−C8−C9 = 130.0(2), C17−C18−C19 = 127.5(2), C8−C9−C10 = 109.2(2), C18−C19−C20 = 110.8(2), C8−C9−C19 = 115.8(2), C18−C19−C9 = 109.6(2), C9−C19−C20 = 111.1(2), C19−C9−C10 = 112.7(2).

at δ 6.03 (^3J(6-H, 7-H) = 15.8 Hz). The 8-H and 9-H hydrogen resonances are found at δ 5.93/δ 5.55 (^3J(8-H, 9-H) = 15.2 Hz) and the 9-CH_3 signal at δ 1.56. The hafnium system **10a** shows analogous solid-state photochemical behavior. Irradiation of the corresponding 4:4:1 mixture of the geometrical isomers eventually led to a sample highly enriched in *E*,*E*;*E*,*E*-**10a** with only traces of the other two residual isomers detectable.

Photolysis of the 4:4:1 mixture of the three (Cp-pentadienyl)$_2$$ZrCl_2$ **9a** isomers in dichloromethane (HPK 125, Pyrex filter) for 2 h at room temperature resulted in the formation of a 1:3.3 mixture of the pair of isomeric formal [4 + 4] cycloaddition products Me_2-*cis*-**12a** and Me_2-*trans*-**12a** (see Scheme 10). The NMR spectra of both systems show a cis-1,2-substitution pattern of the Cp rings at the newly formed nonplanar doubly unsaturated eight-membered carbocycle. In Me_2-*cis*-**12a** the methyl substituents are attached cis to each other and (according to the detailed NMR analysis; see the Supporting Information for details) cis to the Cp substituents. Consequently, the methyl groups in Me_2-*trans*-**12a** are attached trans to each other at the cyclooctadienylene ansa bridge. The structual assignment of the Me_2-*trans*-**12a** was supported by the X-ray crystal structure analysis of the compound (see below).

Photolysis of the pure *E*,*E*;*E*,*E*-**9a** isomer under similar conditions in d_8-toluene gave the [4 + 4] cycloaddition products Me_2-*cis*-**12a** and Me_2-*trans*-**12a** in the same ratio (1:3.3). The (Cp-pentadienyl)$_2$$HfCl_2$ system reacted analogously upon photolysis. Irradiation of the 4:4:1 mixture of the three **10a** isomers gave a 1:4 mixture of the dimethyl-substituted cyclooctadienylene-bridged *ansa*-hafnocene complexes Me_2-*cis*-**13a** and Me_2-*trans*-**13a** (see Scheme 10). The latter compound was also characterized by X-ray diffraction. Again, photolysis of the pure *E*,*E*;*E*,*E*-**10a** isomer led to the same product mixture. The photolysis reaction of the hafnium system is slightly complicated by the formation of increasing amounts of as yet not positively identified follow-up products upon prolonged photolysis of the samples. The observed Me_2-*cis*-:Me_2-*trans* ratios theoretically correlate with an overall dienyl *E*:*Z* ratios of 62:38 (Zr) and 60:40 (Hf), respectively.

Scheme 11



The photolysis reaction of the (Cp-hexadienyl)$_2$MCl$_2$ zirconium and hafnium complexes (**9b**, **10b**) proceeded analogously. Irradiation of the mixtures of the three isomers in the solid state in both cases resulted in a rapid cis/trans isomerization to take place, which eventually made the pure *E*,*E*;*E*,*E*-**9b** (Zr) and *E*,*E*;*E*,*E*-**10b** (Hf) isomers available.

Photolysis of the 6:4:1 (Zr) or 8:5:1 (Hf) mixture of the three respective (Cp-hexadienyl)$_2$MCl$_2$ isomers in solution (CH$_2$Cl$_2$) resulted in the formation of 1:5 (Zr) or 1:6 (Hf) mixtures of the respective [4 + 4] photocycloaddition products Et$_2$-*cis*-/Et$_2$-*trans*-**12b** (Zr) and Et$_2$-*cis*-/Et$_2$-*trans*-**13b** (Hf). Their structures were derived by a close comparison of their typical spectroscopic data with those of the systems **12a**/**13a** (see above and Scheme 10).

Structural Characterization of the [4 + 4] Photocycloaddition Products. Crystals of the complex Me$_2$-*trans*-**12a** suitable for the X-ray crystal structure analysis were obtained from a toluene solution of the mixture of [4 + 4] cycloaddition products upon cooling (see Figure 7). The structure shows that a bridging cyclooctadienylene system had been formed in the photolysis reaction. The zirconocene is characterized by a Cp(centroid)−Zr−Cp(centroid) angle of 124.1°. The Zr−C(Cp) bond lengths are found within a small range of 2.470(2)−2.527(2) Å. The newly formed cyclooctadiene ring features a slightly twisted boat conformation.[15] The metallocene Cp rings were found 1,2-cis attached at the cyclooctadiene C6−C16 single bond. The methyl substituents are arranged trans to each other at C9 and C19. The latter is found cis to the Cp rings.

The hafnium complex Me$_2$-*trans*-**13a** is almost isostructural with Me$_2$-*trans*-**12a**. Its structure is depicted in the Supporting Information.

Conclusions

The systems described in this account show the typical features that one would expect for dynamic topochemical reactions, including their characteristic inverted behavior relative to conventional topochemical reactions. The latter typically show photochemical cycloaddition reactions controlled by their molecular orientation in the crystal lattice, a behavior which necessarily breaks down in solution. In contrast to this, our systems feature fixed conformational arrangements in the solid state that have the pairs of double bonds within these molecules efficiently separated so far from each other at the open front side of the bent metallocene wedge that any photochemical cycloaddition is effectively prevented as long as this conformationally fixed situation persists. Consequently, we see other reactions than cycloaddition to occur upon photolysis in the solid state.

The situation changes upon bringing these systems into solution. Now a very effective and rapid conformational equilibration of the bent-metallocene rotamers takes place which may bring the intramolecular pairs of C═C double bonds attached at the bent-metallocene framework into close proximity and a favorable relative orientation for the photochemical cycloaddition reaction can occur. During this process the stereochemical information present at the pendant C═C double bond side chains is in most cases not carried through to the product. This may indicate the possibility of rotational scrambling at some intermediate stage of the reaction, as is formally sketched in Scheme 11. From previous detailed mechanistic studies we know that the formal [4 + 4] cycloaddition reaction of the (Cp-butadienyl)$_2$ZrCl$_2$ system proceeds stepwise with initial [2 + 2] cycloaddition at the distal C═C double bonds followed by conformational equilibration and a final thermally induced Cope rearrangement.[16] Therefore, a tentative formal description of the stereochemical scrambling taking place at a respective intermediate stage (**15**) might be followed from that study, although the mechanistic details of the photochemical steps of the cycloaddition sequences need to be clarified.[17]

The remarkable features of the dynamic topochemical reaction control have here been used to add an attractive and useful tool to synthetic metallocene chemistry. It has made new types of *ansa*-metallocene precursors for homogeneous Ziegler−Natta olefin polymerization catalysts[18] easily available. It is quite conceivable that similar properties may lead to the development of related systems at conformatively flexible organic frameworks that will lead to new applications of the principle of dynamic topochemical reaction control in organic synthesis as well.

Experimental Section

General Procedures. Reactions with air- and water-sensitive compounds were carried out under argon using Schlenk-type glassware or in a glovebox. Solid compounds were collected on sintered-glass frits and washed with appropriate solvents before being dried under vacuum. Solvents were dried and

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(15) Rocha, W. R.; De Almeida, W. B. *J. Comput. Chem.* **1997**, *18*, 254–259.

(16) Paradies, J.; Greger, I.; Kehr, G.; Erker, G.; Bergander, K.; Fröhlich, R. *Angew. Chem.* **2006**, *118*, 7792−7795; *Angew. Chem., Int. Ed.* **2006**, *45*, 7630−7633.

(17) See for comparison: Bartlett, P. D.; Montgomery, L. K.; Seidel, B. *J. Am. Chem. Soc.* **1964**, *86*, 622–628. Bartlett, P. D.; Montgomery, L. K. *J. Am. Chem. Soc.* **1964**, *86*, 628–631.

(18) Greger, I.; Kehr, G.; Fröhlich, R.; Erker, G. *Organometallics* **2010**, *29*, 860–866. Paradies, J.; Kehr, G.; Fröhlich, R.; Erker, G. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15333–15337.

distilled under argon prior to use. 6-Ethylfulvene, 6-propylfulvene (**3a,b**), 6-(phenylethyl)fulvene (**3c**), and (((*E*)-2-phenyl-1-propenyl)cyclopentadienyl)lithium (**5c**) were prepared as described in the literature.[8,10] The fulvenes **7a** and **7b** were prepared in analogy to a literature procedure[13] (for details see the Supporting Information). The following instruments were used for physical characterization of the compounds. Elemental analyses: Foss-Heraeus CHNO-Rapid. NMR: Varian UNITY plus NMR spectrometer (^{1}H, 599.7 MHz; ^{13}C, 150.8 MHz), Varian 500 MHz INOVA (^{1}H, 499.8 MHz; ^{13}C, 125.7 MHz). Assignments of the resonances were supported by 2D experiments. X-ray diffraction: data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius BV, 1998), data reduction Denzo-SMN,[19] absorption correction SORTAV[20] and Denzo,[21] structure solution SHELXS-97,[22] structure refinement SHELXL-97,[23] and graphics XP (BrukerAXS, 2000). Thermal ellipsoids in all figures are drawn at the 50% probability level. R1 values are given for observed reflections and wR2 values for all reflections.

Preparation of ((1-Propenyl)cyclopentadienyl)lithium (*E*-/*Z*-5a). LDA (1.71 g, 16 mmol) was dissolved in tetrahydrofuran (100 mL) and cooled to −78 °C. A solution of 6-ethylfulvene (**3a**; 1.7 g, 16 mmol) in tetrahydrofuran (10 mL) was added, and the reaction mixture was warmed to room temperature within 5 h. The solvent was removed in vacuo, and the remaining solid was treated with diethyl ether (30 mL) and precipitated with pentane (30 mL). The white product was filtered, washed with pentane, and dried under vacuum. The product was formed as a mixture of ((*E*)-(1-propenyl)-cyclopentadienyl)- and ((*Z*)-(1-propenyl)cyclopentadienyl)lithium (1.62 g, 14.5 mmol, 90%) in a ratio of about 86:14. ***E*-5a**: ^{1}H NMR (600 MHz, d_8-THF, 298 K) δ 6.25 (dq, $^3J_{H,H}$ = 15.4 Hz, $^4J_{H,H}$ = 1.7 Hz, 1H, 6-H), 5.75 (m, 2H, 2-H, 5-H), 5.60 (m, 2H, 3-H, 4-H), 5.41 (dq, $^3J_{H,H}$ = 15.4 Hz, $^3J_{H,H}$ = 6.5 Hz, 1H, 7-H), 1.70 (dd, $^3J_{H,H}$ = 6.5 Hz, $^4J_{H,H}$ = 1.7 Hz, 3H, 8-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-THF, 298 K) δ 131.5 (C6), 119.3 (C1), 110.3 (C7), 104.2 (C3, C4), 102.6 (C2, C5), 18.6 (C8) ppm. ***Z*-5a**: ^{1}H NMR (600 MHz, d_8-THF, 298 K) δ 6.28 (dq, $^3J_{H,H}$ = 11.2 Hz, $^4J_{H,H}$ = 1.6 Hz, 1H, 6-H), 5.84, 5.69 (each m, each 2H, C_5H_4), 4.84 (dq, $^3J_{H,H}$ = 11.2 Hz, $^3J_{H,H}$ = 6.9 Hz, 1H, 7-H), 1.84 (dd, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 1.6 Hz, 3H, 8-H) ppm. ^{13}C{^{1}H} NMR (151 MHz, d_8-THF, 298 K) δ 130.3 (C6), 110.5 (C7), 106.3, 104.6 (C_5H_4), 15.5 (C8), n.o. (C1) ppm.

Preparation of (((*E*)-1-Butenyl)cyclopentadienyl)lithium (*E*/*Z*-5b). LDA (1.16 g, 10.8 mmol) was dissolved in tetrahydrofuran (100 mL) and cooled to −78 °C. A solution of 6-propylfulvene (**3b**; 1.16 g, 9.8 mmol) in tetrahydrofuran (10 mL) was added, and the reaction mixture was warmed to room temperature within 2 h. The solvent was removed and the remaining solid was suspended in pentane (40 mL). The white product (0.91 g, 7.2 mmol, 74%) was filtered, washed with pentane, and dried under vacuum. The product was formed as nearly pure ((*E*)-(1-butenyl)cyclopentadienyl)lithium with only traces of the *Z* isomer (*E*:*Z* = 95:5). ***Z*-5b**: ^{1}H NMR (600 MHz, d_8-THF, 298 K) δ 6.22 (d, $^3J_{H,H}$ = 11.2 Hz, 1H, 6-H), 5.82 (m, 2H, 2-H, 5-H), 5.68 (m, 2H, 3-H, 4-H), 4.72 (dt, $^3J_{H,H}$ = 11.2 Hz, $^3J_{H,H}$ = 6.6 Hz, 1H, 7-H), 2.37 (dq, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,H}$ = 6.6 Hz, 2H, 8-H), 1.03 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, 9-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-THF, 298 K) δ 128.6 (C6), n.o. (C1), 119.5 (C7), 106.3, 104.6 (C_5H_4), 23.4 (C8), 15.2 (C9) ppm. ***E*-5b**: ^{1}H NMR (600 MHz, d_8-THF, 298 K) δ 6.24 (d, $^3J_{H,H}$ = 15.4 Hz, 1H, 6-H), 5.77 (m, 2H, 2-H, 5-H), 5.61 (m, 2H, 3-H, 4-H), 5.47 (dt, $^3J_{H,H}$ = 15.4 Hz, $^3J_{H,H}$ = 6.7 Hz, 1H, 7-H), 2.07 (dq, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,H}$ = 6.7 Hz, 2H, 8-H), 0.99 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, 9-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-THF, 298 K) δ 129.4 (C6), 119.2 (C1), 118.3 (C7), 104.3 (C3, C4), 102.8 (C2, C5), 27.2 (C8), 15.5 (C9) ppm.

Preparation of ((1,3-Pentadienyl)cyclopentadienyl)potassium (*E,E*/*E,Z*-8a). KHMDS (2.0 g, 10.1 mmol) was dissolved in diethyl ether (80 mL). A solution of 6-(*trans*-1-butenyl)fulvene (**7a**; 1.33 g, 10.1 mmol) in diethyl ether (10 mL) was added slowly at 0 °C, and the reaction mixture was stirred for another 2 h at room temperature. The solvent was removed, and the remaining solid was suspended in pentane (50 mL). The yellow product was filtered, washed several times with pentane, and dried under vacuum. This way a mixture of *E,E*- and *E,Z*-**8a** (1.64 g, 9.6 mmol, 95%) with a ratio of 55:45 was obtained. ***E,E*-8a**: ^{1}H NMR (600 MHz, d_8-THF, 298 K) δ 6.28 (d, $^3J_{H,H}$ = 14.9 Hz, 1H, 6-H), 6.04 (ddm, $^3J_{H,H}$ = 14.2 Hz, $^3J_{H,H}$ = 10.4 Hz, 1H, 8-H), 5.98 (dd, $^3J_{H,H}$ = 14.9 Hz, $^3J_{H,H}$ = 10.4 Hz, 1H, 7-H), 5.72 (m, 2H, 2-H, 5-H), 5.58 (m, 2H, 3-H, 4-H), 5.19 (dq, $^3J_{H,H}$ = 14.2 Hz, $^3J_{H,H}$ = 6.8 Hz, 1H, 9-H), 1.70 (dd, $^3J_{H,H}$ = 6.8 Hz, $^5J_{H,H}$ = 1.2 Hz, 3H, 10-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-THF, 298 K) δ 136.1 (C8), 132.4 (C6), 120.2 (C1), 116.9 (C9), 115.5 (C7), 107.8 (C3, C4), 105.8 (C2, C5), 18.4 (C10) ppm. ***E,Z*-8a**: ^{1}H NMR (600 MHz, d_8-THF, 298 K) δ 6.36 (d, $^3J_{H,H}$ = 15.0 Hz, 1H, 6-H), 6.25 (dd, $^3J_{H,H}$ = 15.0 Hz, $^3J_{H,H}$ = 10.9 Hz, 1H, 7-H), 5.98 (m, 1H, 8-H), 5.78 (m, 2H, 2-H, 5-H), 5.61 (m, 2H, 3-H, 4-H), 4.86 (dq, $^3J_{H,H}$ = 10.5 Hz, $^3J_{H,H}$ = 7.0 Hz, 1H, 9-H), 1.72 (dd, $^3J_{H,H}$ = 7.0 Hz, $^5J_{H,H}$ = 1.5 Hz, 3H, 10-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-THF, 298 K) δ 134.4 (C6), 134.0 (C8), 120.4 (C1), 114.0 (C9), 110.7 (C7), 108.2 (C3, C4), 106.3 (C2, C5), 13.4 (C10) ppm.

Preparation of ((1,3-Hexadienyl)cyclopentadienyl)potassium (*E,E*/*E,Z*-8b). KHMDS (1.39 g, 7.0 mmol) was dissolved in diethyl ether (50 mL). A solution of 6-(*trans*-1-pentenyl)fulvene (**7b**; 1.39 g, 7.0 mmol) in diethyl ether (10 mL) was added slowly at 0 °C, and the reaction mixture was stirred for another 2 h at room temperature. The solvent was removed, and the remaining solid was suspended in pentane (40 mL). The yellow product was filtered, washed several times with pentane, and dried under vacuum. In this way a mixture of *E,E*- and *E,Z*-**8b** (1.1 g, 6.0 mmol, 86%) with a ratio of 71:29 was obtained. ***E,E*-8b**: ^{1}H NMR (600 MHz, d_8-THF, 298 K) δ 6.29 (d, $^3J_{H,H}$ = 14.7 Hz, 1H, 6-H), 6.03 (ddm, $^3J_{H,H}$ = 14.4 Hz, $^3J_{H,H}$ = 10.6 Hz, 1H, 8-H), 5.97 (dd, $^3J_{H,H}$ = 14.7 Hz, $^3J_{H,H}$ = 10.6 Hz, 1H, 7-H), 5.72 (m, 2H, 2-H, 5-H), 5.58 (m, 2H, 3-H, 4-H), 5.24 (dt, $^3J_{H,H}$ = 14.4 Hz, $^3J_{H,H}$ = 6.7 Hz, 1H, 9-H), 2.06 (m, 2H, 10-H), 0.98 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, 11-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-THF, 298 K) δ 134.0 (C8), 132.7 (C6), 124.8 (C9), 120.2 (C1), 115.5 (C7), 107.9 (C3, C4), 105.8 (C2, C5), 26.8 (C10), 15.1 (C11) ppm. ***E,Z*-8b**: ^{1}H NMR (600 MHz, d_8-THF, 298 K) δ 6.36 (d, $^3J_{H,H}$ = 14.9 Hz, 1H, 6-H), 6.23 (dd, $^3J_{H,H}$ = 14.9 Hz, $^3J_{H,H}$ = 10.9 Hz, 1H, 7-H), 5.93 (tm, $^3J_{H,H}$ = 10.9 Hz, 1H, 8-H), 5.76 (m, 2H, 2-H, 5-H), 5.61 (m, 2H, 3-H, 4-H), 4.82 (dt, $^3J_{H,H}$ = 10.9 Hz, $^3J_{H,H}$ = 7.3 Hz, 1H, 9-H), 2.19 (m, 2H, 10-H), 0.99 (t, $^3J_{H,H}$ = 7.5 Hz, 3H, 11-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-THF, 298 K) δ 134.6 (C6), 132.5 (C8), 122.5 (C9), 120.4 (C1), 110.8 (C7), 108.2 (C3, C4), 106.3 (C2, C5), 21.8 (C10), 15.2 (C11) ppm.

Metallocene Complexes. Procedure. Throughout the procedure the compounds have to be kept in the dark to avoid a photochemical reaction. The alkali-metal salt of the ligand and $MCl_4(THF)_2$ (M = Zr, Hf) were put together in a Schlenk flask in a 2:1 ratio and cooled to −78 °C. Precooled THF was added slowly, and the stirred mixture was warmed to room temperature overnight. The THF was removed in vacuo, and the same amount of dichloromethane or toluene was added. The resulting suspension was filtered through Celite to remove the alkali-metal chloride. The solid was washed with several portions of dichloromethane or toluene until the portion remained colorless. The filtrate was evaporated to dryness, and the resulting crude product was suspended in pentane, filtered, and dried under vacuum.

Preparation of Bis[(1-propenyl)cyclopentadienyl]zirconium Dichloride (*E,E*-/*E,Z*-/*Z,Z*-6a). From the reaction of the isomeric mixture of **5a** (1.0 g, 8.9 mmol) and bis(tetrahydrofuran)zirconium tetrachloride (1.7 g, 4.5 mmol) in THF (70 mL) and workup using

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toluene a light yellow solid (890 mg, 2.4 mmol, 53%) was isolated. The ratio of *E*,*Z*- to *E*,*Z*- to *Z*,*Z*-complex was 18:7:1. Crystals of **_E,E_-6a** suitable for X-ray diffraction were obtained from a toluene solution of the isomeric mixture upon cooling. Anal. Calcd for $C_{16}H_{18}Cl_2Zr$ (372.4 g/mol): C, 51.60; H, 4.87. Found: C, 51.46; H, 4.58. Characteristic data are as follows. **_E,E_-6a**: ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ 6.37, 6.29 (each m, C_5H_4), 6.10 (dq, $^{3}J_{H,H}$ = 15.8 Hz, $^{3}J_{H,H}$ = 6.6 Hz, 7-H), 1.89 (dd, $^{3}J_{H,H}$ = 6.6 Hz, $^{5}J_{H,H}$ = 1.7 Hz, 8-H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K) δ 129.2 (C7), 128.9 (C1), 124.11 (C6), 115.0, 114.87 (C_5H_4), 18.6 (C8). **_E,Z_-6a**: ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ 6.44/6.34, 6.37/6.30 (each m, C_5H_4), 6.11 (dq, $^{3}J_{H,H}$ = 15.8 Hz, $^{3}J_{H,H}$ = 6.6 Hz), 5.84 (dq, $^{3}J_{H,H}$ = 11.4 Hz, $^{3}J_{H,H}$ = 7.2 Hz) (7-H), 1.927 (dd, $^{3}J_{H,H}$ = 7.2 Hz, $^{5}J_{H,H}$ = 1.8 Hz), 1.89 (dd, $^{3}J_{H,H}$ = 6.6 Hz, $^{5}J_{H,H}$ = 1.7 Hz) (8-H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K) δ 129.4, 128.6 (C7), 128.7, 127.7 (C1), 124.06, 123.41 (C6), 117.7, 115.0, 114.85, 114.8 (C_5H_4), 18.6, 15.3 (C8). **_Z,Z_-6a**: ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) δ 6.46, n.o. (m, C_5H_4), 5.85 (dq, $^{3}J_{H,H}$ = 11.4 Hz, $^{3}J_{H,H}$ = 7.2 Hz, 7-H), 1.932 (dd, $^{3}J_{H,H}$ = 7.2 Hz, $^{5}J_{H,H}$ = 1.8 Hz, 8-H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K) δ 123.37 (C6).

X-ray Crystal Structure Analysis of _E,E_-6a: M_r = 372.42 g/mol, yellow crystal 0.30 × 0.20 × 0.10 mm, a = 14.2011(5) Å, b = 6.6487(2) Å, c = 16.7868(6) Å, β = 97.411(2)°, V = 1571.75(9) Å^3, ρ_{calcd} = 1.574 g cm^{-3}, μ = 1.023 mm^{-1}, empirical absorption correction (0.749 ≤ T ≤ 0.896), Z = 4, monoclinic, space group $C2/c$ (No. 15), λ = 0.710 73 Å, T = 223(2) K, ω and φ scans, 12 961 reflections collected (±h, ±k, ±l), (sin θ)/λ = 0.67 Å^{-1}, 1953 independent (R_{int} = 0.023) and 1852 observed reflections ($I \geq 2\sigma(I)$), 117 refined parameters, R1 = 0.020, wR2 = 0.056, maximum (minimum) residual electron density 0.34 (−0.22) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms; group C6−C7−C8 refined with split positions.

Preparation of Bis[(_E_-1-butenyl)cyclopentadienyl]zirconium Dichloride (_E,E_-6b). From the reaction of *E*-**5b** (440 mg, 3.49 mmol) and bis(tetrahydrofuran)zirconium tetrachloride (658 mg, 1.75 mmol) in THF (40 mL) and workup using toluene a yellow solid (380 mg,0.95 mmol, 55%) was isolated. Crystals suitable for X-ray diffraction were obtained from a toluene solution upon cooling. Anal. Calcd for $C_{18}H_{22}Cl_2Zr$ (400.5 g/mol): C, 53.98; H, 5.54. Found: C, 53.82; H, 5.60. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 6.36 (m, 4H, 2-H, 5-H), 6.29 (m, 4H, 3-H, 4-H), 6.22 (dt, $^{3}J_{H,H}$ = 15.8 Hz, $^{4}J_{H,H}$ = 1.4 Hz, 2H, 6-H), 6.14 (dt, $^{3}J_{H,H}$ = 15.8 Hz, $^{3}J_{H,H}$ = 6.3 Hz, 2H, 7-H), 2.24 (qdd, $^{3}J_{H,H}$ = 7.5 Hz, $^{3}J_{H,H}$ = 6.3 Hz, $^{3}J_{H,H}$ = 1.4 Hz, 4H, 8-H), 1.08 (t, $^{3}J_{H,H}$ = 7.5 Hz, 6H, 9-H) ppm. ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ 136.1 (C7), 128.8 (C1), 122.0 (C6), 115.2 (C3, C4), 114.8 (C2, C5), 26.3 (C8), 13.8 (C9) ppm.

Preparation of Bis[(1,3-pentadienyl)cyclopentadienyl]zirconium Dichloride (_E,E;E,E-/E,E;E,Z-/E,Z;E,Z_-9a). From the reaction of the isomeric mixture of **8a** (520 mg, 3.05 mmol) and bis(tetrahydrofuran)zirconium tetrachloride (576 mg, 1.53 mmol) in THF (40 mL) and workup using toluene a yellow solid (460 mg, 1.1 mmol, 71%) was isolated. The ratio of *E*,*E*;*E*,*E*-**9a** to *E*,*E*;*E*,*Z*-**9a** to *E*,*Z*;*E*,*Z*-**9a** was 4:4:1. Anal. Calcd for $C_{20}H_{22}Cl_2Zr$ (424.5 g/mol): C, 56.59; H, 5.22. Found: C, 56.98; H, 5.07. Characteristic data are as follows. **_E,E/E,E_-9a**: ^{1}H NMR (600 MHz, d_8-toluene, 298 K) δ 6.34 (dd, $^{3}J_{H,H}$ = 15.8 Hz, $^{3}J_{H,H}$ = 10.7 Hz, 7-H), 6.03 (d, $^{3}J_{H,H}$ = 15.8 Hz, 6-H), 5.98 (m, 2-H, 5-H), 5.93 (ddm, $^{3}J_{H,H}$ = 15.2 Hz, $^{3}J_{H,H}$ = 10.7 Hz, 8-H), 5.81 (m, 3-H, 4-H), 5.55 (dqm, $^{3}J_{H,H}$ = 15.2 Hz, $^{3}J_{H,H}$ = 6.9 Hz, 9-H), 1.56 (dm, $^{3}J_{H,H}$ = 6.9 Hz, 10-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 298 K) δ 132.1 (C8), 131.9 (C7), 130.9 (C9), 122.9 (C6), 18.314 (C10) ppm. **_E,E/E,Z_-9a**: ^{1}H NMR (600 MHz, d_8-toluene, 298 K) δ 6.75 (dd, $^{3}J_{H,H}$ = 15.5 Hz, $^{3}J_{H,H}$ = 11.1 Hz), 6.34 (dd, $^{3}J_{H,H}$ = 15.7 Hz, $^{3}J_{H,H}$ = 10.5 Hz) (7-H), 6.11 (d, $^{3}J_{H,H}$ = 15.5 Hz), 6.01 (d, $^{3}J_{H,H}$ = 15.7 Hz) (6-H), 6.00, 5.97, 5.804, 5.799 (each m, C_5H_4), 5.55 (dqm, $^{3}J_{H,H}$ = 15.1 Hz, $^{3}J_{H,H}$ = 6.8 Hz), 5.38 (dqm) (9-H, $^{3}J_{H,H}$ = 10.7 Hz, $^{3}J_{H,H}$ = 6.8 Hz), 1.62 (dm, $^{3}J_{H,H}$ = 6.8 Hz), 1.55 (dm, $^{3}J_{H,H}$ = 6.8 Hz) (10-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 298 K) δ 132.04, 129.8 (C8), 132.01, 126.8 (C7), 131.0, 127.8 (C9), 122.8, 124.83 (C6), 18.306, 13.58 (C10) ppm.

Preparation of Bis[(1,3-pentadienyl)cyclopentadienyl]hafnium Dichloride (_E,E;E,E-/E,E;E,Z-/E,Z;E,Z_-10a). From the reaction of the isomeric mixture of **8a** (500 mg, 2.9 mmol) and bis(tetrahydrofuran)hafnium tetrachloride (680 mg, 1.45 mmol) in THF (40 mL) and workup using dichloromethane a white solid (460 mg, 0.90 mmol, 62%) was isolated. The ratio of *E*,*E*;*E*,*E*-**10a** to *E*,*E*;*E*,*Z*-**10a** to *E*,*Z*;*E*,*Z*-**10a** was 4:4:1. Anal. Calcd for $C_{20}H_{22}Cl_2Hf$ (511.8 g/mol): C, 46.94, H, 4.33. Found: C, 46.16; H, 4.33. Characteristic data are as follows. **_E,E/E,E_-10a**: ^{1}H NMR (600 MHz, d_8-toluene, 298 K) δ 6.31 (dd, $^{3}J_{H,H}$ = 15.7 Hz, $^{3}J_{H,H}$ = 10.5 Hz, 2H, 7-H), 6.05 (d, $^{3}J_{H,H}$ = 15.7 Hz, 2H, 6-H), 5.95 (ddm, $^{3}J_{H,H}$ = 15.0 Hz, 10.5 Hz, 2H, 8-H), 5.89, 5.73 (each m, C_5H_4), 5.54 (dqm, $^{3}J_{H,H}$ = 15.0 Hz, $^{3}J_{H,H}$ = 6.8 Hz, 9-H), 1.58 (dm, $^{3}J_{H,H}$ = 6.8 Hz, 10-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 298 K) δ 132.1 (C8), 131.8 (C7), 130.7 (C9), 122.9 (C6), 113.58, 113.32 (C_5H_4),18.283 (C10) ppm. **_E,E/E,Z_-10a**: ^{1}H NMR (600 MHz, d_8-toluene, 298 K) δ 6.72 (dd, $^{3}J_{H,H}$ = 15.4 Hz, $^{3}J_{H,H}$ = 11.3 Hz), 6.31 (dd, $^{3}J_{H,H}$ = 15.5 Hz, $^{3}J_{H,H}$ = 10.5 Hz) (7-H), 6.14 (d, $^{3}J_{H,H}$ = 15.4 Hz), 6.04 (d, $^{3}J_{H,H}$ = 15.5 Hz) (6-H), 5.91, 5.88, 5.720, 5.715 (each m, C_5H_4), 5.54 (dqm, $^{3}J_{H,H}$ = 15.0 Hz, $^{3}J_{H,H}$ = 6.8 Hz), 5.38 (dqm, $^{3}J_{H,H}$ = 10.6 Hz, $^{3}J_{H,H}$ = 7.0 Hz) (9-H), 1.63 (dm, $^{3}J_{H,H}$ = 7.0 Hz), 1.57 (dm, $^{3}J_{H,H}$ = 6.8 Hz, 10-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 298 K) δ 132.0, 129.73 (C8), 131.9, 126.7 (C7), 130.7, 127.6 (C9), 122.8, 124.84 (C6), 113.88, 113.57, 113.32, 113.30 (C_5H_4), 18.275, 13.5 (C10) ppm. **_E,Z/E,Z_-10a**: ^{1}H NMR (600 MHz, d_8-toluene, 298 K) δ 6.71 (dd, $^{3}J_{H,H}$ = 15.6 Hz, $^{3}J_{H,H}$ = 11.3 Hz, 7-H), 6.13 (d, $^{3}J_{H,H}$ = 15.4 Hz, 6-H), 5.38 (m, 9-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 298 K) δ 129.67 (C8), 126.8 (C7), 127.7 (C9), 124.80 (C6), 113.87, 113.34 (C_5H_4), 13.6 (C10) ppm.

Preparation of Bis[(1,3-hexadienyl)cyclopentadienyl]zirconium Dichloride (_E,E;E,E-/E,E;E,Z-/E,Z;E,Z_-9b). From the reaction of the isomeric mixture of **8b** (480 mg, 2.6 mmol) and bis(tetrahydrofuran)zirconium tetrachloride (491 mg, 1.3 mmol) in THF (50 mL) and workup using toluene a yellow solid (412 mg, 0.91 mmol, 70%) was isolated. The ratio of *E*,*E*;*E*,*E*-**9b** to *E*,*E*;*E*,*Z*-**9b** to *E*,*Z*;*E*,*Z*-**9b** was 6:4:1. Anal. Calcd for $C_{22}H_{26}Cl_2Zr$ (452.6 g/mol): C, 58.39; H, 5.79. Found: C, 57.96; H, 5.40. Characteristic data are as follows. **_E,E/E,E_-9b**: ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) δ 6.58 (dd, $^{3}J_{H,H}$ = 15.6 Hz, $^{3}J_{H,H}$ = 10.5 Hz, 7-H), 6.42, 6.32 (each m, C_5H_4), 6.28 (d, $^{3}J_{H,H}$ = 15.6 Hz, 6-H), 6.18 (ddm, $^{3}J_{H,H}$ = 15.2 Hz, $^{3}J_{H,H}$ = 10.5 Hz, 8-H), 5.93 (dtm, $^{3}J_{H,H}$ = 15.2 Hz, $^{3}J_{H,H}$ = 6.7 Hz, 9-H), 2.18 (m, 10-H), 1.05 (t, $^{3}J_{H,H}$ = 7.6 Hz, 11-H) ppm. ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K) δ 139.29 (C9), 132.6 (C7), 129.3 (C8), 128.5 (C1), 122.6 (C6), 26.2 (C10), 13.5 (C11) ppm. **_E,E/E,Z_-9b**: ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) δ 6.88 (ddm, $^{3}J_{H,H}$ = 15.9 Hz, $^{3}J_{H,H}$ = 11.2 Hz), 6.58 (dd, $^{3}J_{H,H}$ = 15.5 Hz, $^{3}J_{H,H}$ = 10.5 Hz) (7-H), 6.35 (d, $^{3}J_{H,H}$ = 15.9 Hz), 6.28 (d, $^{3}J_{H,H}$ = 15.5 Hz) (6-H), 6.18 (ddm, $^{3}J_{H,H}$ = 15.2 Hz, $^{3}J_{H,H}$ = 10.5 Hz), 6.09 (tm, $^{3}J_{H,H}$ = 10.9 Hz) (8-H), 5.93 (dtm, $^{3}J_{H,H}$ = 15.2 Hz, $^{3}J_{H,H}$ = 6.7 Hz), 5.59 (dtm, $^{3}J_{H,H}$ = 10.9 Hz, $^{3}J_{H,H}$ = 7.3 Hz) (9-H), 2.30, 2.18 (each m, 10-H), 1.044, 1.043 (each tm, each $^{3}J_{H,H}$ = 7.4 Hz, 11-H) ppm. ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K) δ 139.34, 136.59 (C9), 132.7, 127.48 (C7), 129.2, 127.81 (C8), 124.49, 122.5 (C6), 26.2, 21.7 (C10), 14.41, 13.5 (C11) ppm. **_E,Z/E,Z_-9b**: ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) δ 6.35 (d, $^{3}J_{H,H}$ = 15.8 Hz, 6-H), 6.88 (m, 7-H), 5.38 (m, 9-H) ppm. ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K) δ 136.6 (C9), 127.55 (C7), 127.77 (C8), 124.47 (C6), 21.7 (C10), 14.40 (C11) ppm.

Preparation of Bis[(1,3-hexadienyl)cyclopentadienyl]hafnium Dichloride (_E,E;E,E-/E,E;E,Z-/E,Z;E,Z_-10b). From the reaction of the isomeric mixture of **8b** (170 mg, 0.92 mmol) and bis(tetrahydrofuran)hafnium tetrachloride (214 mg, 0.46 mmol) in THF (20 mL) and workup using toluene a white solid (180 mg, 0.33 mmol, 72%) was isolated. The ratio of *E*,*E*;*E*,*E*-**10b** to *E*,*E*;*E*,*Z*-**10b** to *E*,*Z*;*E*,*Z*-**10b** was 8:5:1. Crystals of *E*,*E*;*E*,*E*-**10b** suitable for X-ray diffraction were obtained from a toluene/pentane solution of the isomeric mixture upon cooling. Anal.

Calcd for $C_{22}H_{26}Cl_2Hf$ (539.8 g/mol): C, 48.95; H, 4.85. Found: C, 49.04; H, 4.80. Characteristic data are as follows. ***E,E*/*E,E*-10b**: ^{1}H NMR (600 MHz, d_8-toluene, 298 K) δ 6.34 (dd, $^3J_{H,H}$ = 15.7 Hz, $^3J_{H,H}$ = 10.5 Hz, 7-H), 6.09 (d, $^3J_{H,H}$ = 15.7 Hz, 6-H), 5.99 (m, 8-H), 5.91 (m, 2-H, 5-H), 5.74 (m, 3-H, 4-H), 5.62 (dt, $^3J_{H,H}$ = 15.2 Hz, $^3J_{H,H}$ = 6.6 Hz, 9-H), 1.95 (m, 10-H), 0.87 (t, $^3J_{H,H}$ = 7.4 Hz, 11-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 298 K) δ 137.8 (C9), 132.0 (C7), 129.74 (C8), 125.9 (C1), 123.1 (C6), 113.6 (C2, C5), 113.3 (C3, C4), 26.2 (C10), 13.60 (C11) ppm. ***E,E*/*E,Z*-10b**: ^{1}H NMR (600 MHz, d_8-toluene, 298 K) δ 6.73 (ddm, $^3J_{H,H}$ = 15.6 Hz, $^3J_{H,H}$ = 11.2 Hz), 6.34 (dd, $^3J_{H,H}$ = 15.7 Hz, $^3J_{H,H}$ = 10.5 Hz) (7-H), 6.14 (d, $^3J_{H,H}$ = 15.6 Hz), 6.08 (d, $^3J_{H,H}$ = 15.7 Hz) (6-H), 5.99, 5.98 (each m, 8-H), 5.92, 5.90, 5.72, 5.72 (each m, C_5H_4), 5.62 (dt, $^3J_{H,H}$ = 15.2 Hz, $^3J_{H,H}$ = 6.6 Hz), 5.35 (dt, $^3J_{H,H}$ = 10.6 Hz, $^3J_{H,H}$ = 7.7 Hz) (9-H), 2.13, 1.95 (each m, 10-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 298 K) δ 137.9, 135.25 (C9), 132.1, 126.9 (C7), 129.69, 128.3 (C8), 124.9, 123.0 (C6), 114.0, 113.55, 113.29, 113.26 (C_5H_4), 26.2, 21.6 (C10), 14.44, 13.59 (C11) ppm. ***E,Z*/*E,Z*-10b**: ^{1}H NMR (600 MHz, d_8-toluene, 298 K) δ 6.72 (ddm, $^3J_{H,H}$ = 15.5 Hz, $^3J_{H,H}$ = 11.1 Hz, 7-H), 6.13 (d, $^3J_{H,H}$ = 15.5 Hz, 6-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 298 K) δ 135.32 (C9), 127.0 (C7), 128.2 (C8), 113.9, 113.29 (C_5H_4), 14.42 (C11) ppm.

X-ray Crystal Structure Analysis of *E,E*;*E,E*-10b: M_r = 539.82 g/mol, light yellow crystal, 0.20 × 0.10 × 0.02 mm, a = 27.6120(7) Å, b = 6.6102(2) Å, c = 12.0125(3) Å, β = 103.162(2)°, V = 2134.93(10) Å^3, ρ_{calcd} = 1.679 g cm^{-3}, μ = 5.138 mm^{-1}, empirical absorption correction (0.426 ≤ T ≤ 0.904), Z = 4, monoclinic, space group Cc (No. 9), λ = 0.710 73 Å, T = 223(2) K, ω and φ scans, 7802 reflections collected (±h, ±k, ±l), (sin θ)/λ = 0.66 Å^{-1}, 3572 independent (R_{int} = 0.043) and 3477 observed reflections ($I \geq 2\sigma(I)$), 245 refined parameters, R1 = 0.034, wR2 = 0.083, maximum (minimum) residual electron density 1.25 (−0.97) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, terminal ethyl groups are disordered.

Solid-State Photolysis. General Procedure. A small sample of the isomeric mixture of the complex was put in a small Schlenk flask and suspended in pentane (3 mL). The pentane was removed in vacuo so that a thin film of solid was formed on the glass wall of the flask. The solid was irradiated for 2 h from two opposite sides with UV light. This way the nearly pure all-*E* isomers could be obtained with only traces of the other isomers.

***E,E*-6a**: ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) δ 6.36 (m, 4H, 2-H, 5-H), 6.29 (m, 4H, 3-H, 4-H), 6.25 (dq, $^3J_{H,H}$ = 15.8 Hz, $^4J_{H,H}$ = 1.6 Hz, 2H, 6-H), 6.10 (dq, $^3J_{H,H}$ = 15.8 Hz, $^3J_{H,H}$ = 6.7 Hz, 2H, 7-H), 1.89 (dd, $^3J_{H,H}$ = 6.7 Hz, $^4J_{H,H}$ = 1.6 Hz, 6H, 8-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K) δ 129.2 (C7), 128.8 (C1), 124.1 (C6), 115.0 (C3, C4), 114.9 (C2, C5), 18.6 (C8) ppm.

***E,E*;*E,E*-9a:** ^{1}H NMR (600 MHz, d_8-toluene, 298 K) δ 6.34 (dd, $^3J_{H,H}$ = 15.8 Hz, $^3J_{H,H}$ = 10.7 Hz, 2H, 7-H), 6.03 (d, $^3J_{H,H}$ = 15.8 Hz, 2H, 6-H), 5.98 (m, 4H, 2-H, 5-H), 5.93 (ddm, $^3J_{H,H}$ = 15.2 Hz, 10.7 Hz, 2H, 8-H), 5.81 (m, 4H, 3-H, 4-H), 5.55 (dqm, $^3J_{H,H}$ = 15.2 Hz, $^3J_{H,H}$ = 6.9 Hz, 2H, 9-H), 1.56 (dm, $^3J_{H,H}$ = 6.9 Hz, 6H, 10-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 298 K) δ 132.1 (C8), 131.9 (C7), 130.9 (C9), 127.5 (C1), 122.9 (C6), 114.79, 114.77 (C_5H_4), 18.3 (C10) ppm.

***E,E*;*E,E*-10a:** ^{1}H NMR (600 MHz, d_8-toluene, 298 K) δ 6.31 (dd, $^3J_{H,H}$ = 15.7 Hz, $^3J_{H,H}$ = 10.5 Hz, 2H, 7-H), 6.05 (d, $^3J_{H,H}$ = 15.7 Hz, 2H, 6-H), 5.95 (ddm, $^3J_{H,H}$ = 15.0 Hz, 10.5 Hz, 2H, 8-H), 5.89 (m, 4H, 2-H, 5-H), 5.73 (m, 4H, 3-H, 4-H), 5.54 (dqm, $^3J_{H,H}$ = 15.0 Hz, $^3J_{H,H}$ = 6.8 Hz, 2H, 9-H), 1.58 (dm, $^3J_{H,H}$ = 6.8 Hz, 6H, 10-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 298 K) δ 132.1 (C8), 131.8 (C7), 130.7 (C9), 125.8 (C1), 122.9 (C6), 113.6 (C2, C5), 113.3 (C3, C4), 18.3 (C10) ppm.

***E,E*;*E,E*-9b:** ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) δ 6.58 (dd, $^3J_{H,H}$ = 15.6 Hz, $^3J_{H,H}$ = 10.5 Hz, 2H, 7-H), 6.42 (m, 4H, 2-H, 5-H), 6.32 (m, 4H, 3-H, 4-H), 6.28 (d, $^3J_{H,H}$ = 15.6 Hz, 2H, 6-H), 6.18 (ddm, $^3J_{H,H}$ = 15.2 Hz, $^3J_{H,H}$ = 10.5 Hz, 2H, 8-H), 5.93 (dtm, $^3J_{H,H}$ = 15.2 Hz, $^3J_{H,H}$ = 6.7 Hz, 2H, 9-H), 2.18 (m, 4H, 10-H), 1.05 (t, $^3J_{H,H}$ = 7.6 Hz, 6H, 11-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K) δ 139.3 (C9), 132.6 (C7), 129.3 (C8), 128.5 (C1), 122.6 (C6), 115.17, 115.16 (C_5H_4), 26.2 (C10), 13.5 (C11) ppm.

***E,E*;*E,E*-10b:** ^{1}H NMR (600 MHz, d_8-toluene, 298 K) δ 6.34 (dd, $^3J_{H,H}$ = 15.7 Hz, $^3J_{H,H}$ = 10.5 Hz, 2H, 7-H), 6.08 (d, $^3J_{H,H}$ = 15.7 Hz, 2H, 6-H), 5.99 (ddm, $^3J_{H,H}$ = 15.2 Hz, $^3J_{H,H}$ = 10.5 Hz, 2H, 8-H), 5.91 (m, 4H, 2-H, 5-H), 5.74 (m, 4H, 3-H, 4-H), 5.62 (dt, $^3J_{H,H}$ = 15.2 Hz, $^3J_{H,H}$ = 6.6 Hz, 2H, 9-H), 1.95 (psquint, 4H, 10-H), 0.87 (t, $^3J_{H,H}$ = 7.4 Hz, 6H, 11-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 298 K) δ 137.8 (C9), 132.0 (C7), 129.7 (C8), 125.9 (C1), 123.1 (C6), 113.6 (C2, C5), 113.3 (C3, C4), 26.2 (C10), 13.6 (C11) ppm.

Photochemical Reactions in Solution. Preparation of [(3,4-Dimethylcyclobutylene)bis(cyclopentadienyl)]zirconium Dichloride (Me$_2$-*cis*-/Me$_2$-*trans*-11a). The isomeric mixture of **6a** (420 mg, 1.13 mmol) was dissolved in dichloromethane (40 mL) and irradiated for 2.5 h (Pyrex filter). Solvent was removed, and the remaining solid was suspended in pentane (15 mL). Filtration and drying of the obtained solid in vacuo gave a Me$_2$-*cis*- to Me$_2$-*trans* mixture of 1.7:1 as a white powder (300 mg, 0.81 mmol, 72%). The same isomeric mixture was obtained by irradiation of a small sample of *E*,*E*-**6a** in d_8-toluene. Crystals of the Me$_2$-*cis* isomer suitable for X-ray diffraction were obtained from a toluene solution of the isomeric mixture upon cooling. Anal. Calcd for $C_{16}H_{18}Cl_2Zr$ (372.4 g/mol): C, 51.60; H, 4.87. Found: C, 51.47; H, 4.95. **Me$_2$-*cis*-11a**: ^{1}H NMR (600 MHz, d_8-toluene, 298 K) δ 6.50 (m, 2H, 3-H), 6.31 (m, 2H, 4-H), 5.79 (m, 2H, 5-H), 5.56 (m, 2H, 2-H), 2.79 (m, 2H, 6-H), 2.30 (m, 2H, 7-H), 0.71 (m, 6H, 8-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 298 K) δ 138.4 (C1), 125.2 (C3), 120.9 (C4), 109.5 (C5), 109.3 (C2), 48.0 (C6), 34.9 (C7), 14.8 (C8) ppm. **Me$_2$-*trans*-11a**: ^{1}H NMR (600 MHz, d_8-toluene, 298 K) δ 6.57 (m, 1H, 4′-H), 6.44 (m, 1H, 3-H), 6.38 (m, 1H, 4-H), 6.21 (m, 1H, 3′-H), 5.81 (m, 1H, 5′-H), 5.69 (m, 1H, 2′-H), 5.65 (m, 1H, 5-H), 5.58 (m, 1H, 2-H), 3.26 (m, 1H, 6′-H), 2.64 (m, 1H, 6-H), 2.17 (m, 1H, 7-H), 1.63 (m, 1H, 7′-H), 0.77 (d, $^3J_{H,H}$ = 6.5 Hz, 3H, 8-H), 0.68 (d, $^3J_{H,H}$ = 7.0 Hz, 3H, 8′-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, d_8-toluene, 298 K) δ 137.8 (C1), 136.0 (C1′), 125.9 (C4′), 124.3 (C3), 122.7 (C4), 119.6 (C3′), 115.6 (C2′), 108.9 (C2), 108.7 (C5), 107.3 (C5′), 48.4 (C6), 46.9 (C6′), 40.5 (C7), 38.7 (C7′), 19.0 (C8), 13.6 (C8′) ppm.

X-ray Crystal Structure Analysis of Me$_2$-*cis*-11a: M_r = 372.42 g/mol, colorless crystal, 0.30 × 0.15 × 0.05 mm, a = 8.2449(2) Å, b = 15.6556(4) Å, c = 11.8931(3) Å, β = 90.727(1)°, V = 1535.02(7) Å^3, ρ_{calcd} = 1.612 g cm^{-3}, μ = 1.048 mm^{-1}, empirical absorption correction (0.744 ≤ T ≤ 0.950), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.710 73 Å, T = 223(2) K, ω and φ scans, 9188 reflections collected (±h, ±k, ±l), (sin θ)/λ = 0.66 Å^{-1}, 3626 independent (R_{int} = 0.042) and 3350 observed reflections ($I \geq 2\sigma(I)$), 174 refined parameters, R1 = 0.044, wR2 = 0.103, maximum (minimum) residual electron density 0.67 (−0.68) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of [(3,4-Diethylcyclobutylene)bis(cyclopentadienyl)]zirconium Dichloride (Et$_2$-*cis*-/Et$_2$-*trans*-11b). *E*,*E*-**6b** (150 mg, 0.37 mmol) was dissolved in dichloromethane (20 mL) and irradiated for 1.5 h (Pyrex filter). The formed precipitate was filtered off through Celite before the solvent was removed, and the remaining solid was suspended in pentane (15 mL). Filtration and drying of the obtained solid in vacuo gave an Et$_2$-*cis*- to Et$_2$-*trans*-**11b** ratio of 1:1.1 as a white powder (120 mg, 0.31 mmol, 83%). Crystals suitable for X-ray diffraction were obtained from a toluene/pentane solution of the isomeric mixture upon cooling. Anal. Calcd for $C_{18}H_{22}Cl_2Zr$ (400.5 g/mol): C, 53.98; H, 5.54. Found: C, 53.87; H, 5.50. **Et$_2$-*cis*-11b**: ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) δ 6.72 (m, 2H, 3-H), 6.56 (m, 2H, 4-H), 6.40 (m, 2H, 5-H), 6.25 (m, 2H, 2-H), 3.64 (m, 2H, 6-H), 2.75 (m, 2H, 7-H), 1.70 (m, 2H, 8-Ha), 1.46 (m, 2H, 8-Hb), 0.88 (t, $^3J_{H,H}$ = 7.4 Hz, 6H, 9-H) ppm; ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K) δ 140.5 (C1), 125.5 (C3), 121.4 (C4), 110.3 (C5), 110.1 (C2), 47.2 (C6), 42.7 (C7), 23.5 (C8), 12.2 (C9) ppm. **Et$_2$-*trans*-11b**: ^{1}H NMR

(600 MHz, CD_2Cl_2, 298 K) δ 6.82 (m, 1H, 4′-H), 6.65 (m, 1H, 3-H), 6.62 (m, 1H, 5′-H), 6.61 (m, 1H, 4-H), 6.44 (m, 1H, 3′-H), 6.36 (m, 1H, 5-H), 6.23 (m, 1H, 2′-H), 6.19 (m, 1H, 2-H), 4.11 (m, 1H, 6′-H), 3.46 (m, 1H, 6-H), 2.86 (m, 1H, 7-H), 2.14 (m, 1H, 7′-H), 1.72 (m, 1H, 8-Ha), 1.65 (m, 1H, 8′-Ha), 1.56 (m, 1H, 8′-Hb), 1.46 (m, 1H, 8-Hb), 0.92 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, 9-H), 0.66 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, 9′-H) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 298 K) δ 140.0 (C1), 137.6 (C1′), 126.3 (C4′), 124.3 (C3), 122.9 (C4), 119.7 (C3′), 116.2 (C2′), 109.93 (C2), 109.86 (C5), 107.8 (C5′), 47.1 (C6, C7), 46.0 (C6′), 44.7 (C7′), 29.2 (C8), 23.1 (C8′), 12.1 (C9), 11.9 (C9′) ppm.

X-ray Crystal Structure Analysis of Et$_2$-*cis*-/Et$_2$-*trans*-11b: M_r = 400.48, colorless, 0.20 × 0.10 × 0.03 mm, a = 12.4775(4) Å, b = 14.3156(5) Å, c = 16.5925(6) Å, α = 76.369(2)°, β = 86.137(2)°, γ = 66.616(1)°, V = 2642.61(16) Å^3, ρ_{calcd} = 1.510 g cm^{-3}, μ = 0.919 mm^{-1}, empirical absorption correction ($0.838 \leq T \leq 0.973$), Z = 6, triclinic, space group $P\bar{1}$ (No. 2), λ = 0.710 73 Å, T = 223(2) K, ω and φ scans, 46 260 reflections collected ($\pm h, \pm k, \pm l$), $(\sin\theta)/\lambda = 0.66$ Å^{-1}, 13 002 independent ($R_{int} = 0.049$) and 6743 observed reflections ($I \geq 2\sigma(I)$), 574 refined parameters, R1 = 0.078, wR2 = 0.247, maximum (minimum) residual electron density 1.25 (−0.84) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms, quality of the crystals was very poor, the accuracy of the refinement with thermal restraints for all atoms besides Zr is limited.

Preparation of [(5,6-Dimethyl-*cis,cis*-3,7-cyclooctadienylene)-bis(cyclopentadienyl)]zirconium Dichloride (Me$_2$-*cis*-/Me$_2$-*trans*-12a). The isomeric mixture of **9a** (400 mg, 0.94 mmol) was dissolved in dichloromethane (40 mL) and irradiated for 2 h (Pyrex filter). Solvent was removed, and the remaining solid was suspended in pentane (10 mL). Filtration and drying of the obtained solid in vacuo gave a Me$_2$-*cis*- to Me$_2$-*trans*-**12a** ratio of 1:3.3 as a yellow powder (348 mg, 0.82 mmol, 87%). The same isomeric mixture was obtained by irradiation of a small sample of *E,E;E,E*-**9a** in d_8-toluene. Crystals of the Me$_2$-*trans* isomer suitable for X-ray diffraction were obtained from a toluene solution of the isomeric mixture upon cooling. Anal. Calcd for $C_{20}H_{22}Cl_2Zr$ (424.5 g/mol): C, 56.59; H, 5.22. Found: C, 56.90; H, 5.11. **Me$_2$-*cis*-12a**: ^1H NMR (600 MHz, d_8-toluene, 298 K) δ 6.46 (m, 2H, 4-H), 6.30 (m, 2H, 3-H), 5.73 (m, 2H, 2-H), 5.38 (m, 2H, 5-H), 5.21 (dm, $^3J_{H,H}$ = 11.6 Hz, 2H, 7-H), 5.10 (dm, $^3J_{H,H}$ = 11.6 Hz, 2H, 8-H), 4.01 (br, 2H, 6-H), 2.52 (m, 2H, 9-H), 0.80 (m, 6H, 10-H) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, d_8-toluene, 298 K) δ 136.8 (C1), 135.8 (C8), 128.3 (C7), 124.8 (C4), 121.4 (C3), 110.5 (C2), 109.2 (C5), 46.2 (C6), 37.9 (C9), 17.2 (C10) ppm. **Me$_2$-*trans*-12a**: ^1H NMR (600 MHz, d_8-toluene, 298 K) δ 6.60 (m, 1H, 4′-H), 6.45 (m, 1H, 3-H), 6.34 (m, 1H, 4-H), 6.15 (m, 1H, 3′-H), 5.85 (m, 1H, 2′-H), 5.60 (ddm, $^3J_{H,H}$ = 11.4 Hz, $^3J_{H,H}$ = 7.5 Hz, 1H, 8′-H), 5.56 (m, 1H, 2-H), 5.49 (m, 1H, 5′-H), 5.43 (m, 1H, 5-H), 5.36 (dd, $^3J_{H,H}$ = 11.4 Hz, $^3J_{H,H}$ = 9.3 Hz, 1H, 7′-H), 4.97 (m, 2H, 7-H, 8-H), 4.28 (m, 1H, 6′-H), 3.83 (d, $^3J_{H,H}$ = 8.0 Hz, 1H, 6-H), 2.26 (m, 1H, 9-H), 1.59 (m, 1H, 9′-H), 0.82 (d, $^3J_{H,H}$ = 6.2 Hz, 3H, 10-H), 0.81 (d, $^3J_{H,H}$ = 6.9 Hz, 3-H, 10′-H) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, d_8-toluene, 298 K) δ 139.1 (C1), 138.5 (C8′), 135.7 (C8), 134.3 (C1′), 131.5 (C7), 127.5 (C4′), 125.8 (C3), 123.9 (C7′), 121.9 (C4), 117.3 (C3′), 112.9 (C2′), 111.6 (C5), 108.1 (C2), 106.7 (C5′), 47.8 (C6), 44.3 (C6′), 42.8 (C9′), 39.2 (C9), 20.2 (C10), 17.7 (C10′) ppm.

X-ray Crystal Structure Analysis of Me$_2$-*trans*-12a. M_r = 424.50 g/mol, light yellow crystal, 0.50 × 0.35 × 0.30 mm, a = 12.6867(2) Å, b = 12.2749(2) Å, c = 13.3417(2) Å, β = 117.529(1), V = 1842.43(5) Å^3, ρ_{calcd} = 1.530 g cm^{-3}, μ = 0.884 mm^{-1}, empirical absorption correction ($0.666 \leq T \leq 0.778$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.710 73 Å, T = 223(2) K, ω and φ scans, 16 537 reflections collected ($\pm h, \pm k, \pm l$), $(\sin\theta)/\lambda$ = 0.67 Å^{-1}, 4502 independent (R_{int} = 0.041) and 3858 observed reflections ($I \geq 2\sigma(I)$), 210 refined parameters, R1 = 0.030, wR2 = 0.078, maximum (minimum) residual electron density 0.57 (−0.59) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of [(5,6-Diethyl-*cis,cis*-3,7-cyclooctadienylene)-bis(cyclopentadienyl)]zirconium Dichloride Et$_2$-*cis*-/Et$_2$-*trans*-12b. The isomeric mixture of **9b** (150 mg, 0.94 mmol) was dissolved in dichloromethane (20 mL) and irradiated for 2 h (Pyrex filter). The resulting precipitate was filtered off through Celite before the solvent was removed, and the remaining solid was suspended in pentane (10 mL). Filtration and drying of the obtained solid in vacuo gave a Et$_2$-*cis*- to Et$_2$-*trans*-**12b** ratio of 1:5 as a yellow solid (131 mg, 0.29 mmol, 88%). The same isomeric mixture was obtained by irradiation of a small sample of *E,E;E,E*-**9b** in d_8-toluene. Anal. Calcd for $C_{22}H_{26}Cl_2Zr$ (452.6 g/mol): C, 58.39; H, 5.79. Found: C, 57.91; H, 5.68. **Et$_2$-*cis*-12b**: ^1H NMR (600 MHz, d_8-toluene, 298 K) δ 6.47 (m, 2H, 4-H), 6.32 (m, 2H, 3-H), 5.78 (m, 2H, 2-H), 5.36 (m, 2H, 5-H), 5.27 (dm, $^3J_{H,H}$ = 11.7 Hz, 2H, 7-H), 5.19 (dm, $^3J_{H,H}$ = 11.7 Hz, 2H, 8-H), 4.12 (m, 2H, 6-H), 2.35 (br, 2H, 9-H), 1.27 (m, 2H, 10-Ha), 1.13 (m, 2H, 10-Hb), 0.84 (t, $^3J_{H,H}$ = 7.2 Hz, 6H, 11-H) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, d_8-toluene, 298 K) δ 136.90 (C1), 134.5 (C8), 128.9 (C7), 124.8 (C4), 121.4 (C3), 110.6 (C2), 109.2 (C5), 46.4 (C6), 44.89 (C9), 24.4 (C10), 13.0 (C11) ppm. **Et$_2$-*trans*-12b**: ^1H NMR (600 MHz, d_8-toluene, 298 K) δ 6.58 (m, 1H, 4′-H), 6.45 (m, 1H, 3-H), 6.34 (m, 1H, 4-H), 6.14 (m, 1H, 3′-H), 5.87 (m, 1H, 2′-H), 5.64 (dd, $^3J_{H,H}$ = 11.3 Hz, $^3J_{H,H}$ = 7.8 Hz, 1H, 8′-H), 5.59 (m, 1H, 2-H), 5.47 (dd, $^3J_{H,H}$ = 11.3 Hz, $^3J_{H,H}$ = 9.5 Hz, 1H, 7′-H), 5.41 (m, 2H, 5-H), 5.40 (m, 2H, 5′-H), 5.12 (dm, $^3J_{H,H}$ = 11.2 Hz, 1H, 7-H), 4.98 (dd, $^3J_{H,H}$ = 11.2 Hz, $^3J_{H,H}$ = 9.1 Hz, 1H, 8-H), 4.40 (m, 1H, 6′-H), 3.99 (dm, $^3J_{H,H}$ = 7.8 Hz, 1H, 6-H), 2.25 (m, 1H, 9-H), 1.64 (m, 1H, 9′-H), 1.51 (m, 1H, 10-Ha), 1.41 (m, 1H, 10′-Ha), 1.15 (m, 1H, 10′-H^b), 0.85 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, 11-H), 0.80 (m, 1H, 10-Hb), 0.76 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, 11′-H) ppm; $^{13}C\{^1H\}$ NMR (151 MHz, d_8-toluene, 298 K) δ 139.2 (C1), 136.9 (C8′), 134.9 (C8), 134.3 (C1′), 133.2 (C7), 127.6 (C4′), 125.8 (C3), 125.4 (C7′), 122.0 (C4), 117.2 (C3′), 113.0 (C2′), 111.7 (C5), 108.2 (C2), 106.6 (C5′), 47.9 (C6), 47.2 (C9′), 44.90 (C6′), 44.7 (C9), 27.6 (C10), 25.8 (C10′), 12.6 (C11), 11.5 (C11′) ppm.

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Supporting Information Available: Text, figures, and tables giving further experimental and spectroscopic details for all compounds and CIF files giving crystallographic data for *E,E*-**6a**, *E,E*-**6b**, *E,E;E,E*-**10b**, Me$_2$-*cis*-**11a,** Et$_2$-*cis*-**11b**/Et$_2$-*trans*-**11b**, Me$_2$-*trans*-**12a**, and Me$_2$-*cis*-**13a**. This material is available free of charge via the Internet at http://pubs.acs.org.