[2+2]-Cycloaddition and Subsequent *meso/rac ansa*-Metallocene Interconversion by Photolysis of a Bis(1,3-dialkenylcyclopentadienyl)zirconium Complex

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6,6-Dimethylfulvene (**5**) was treated with acetone under basic conditions to yield 3-(1-methylethenyl)-6,6-dimethylfulvene (**7**). Deprotonation with LDA followed by transmetalation with 0.5 molar equiv of zirconium tetrachloride gave bis[1,3-di(1-methylethenyl)C$_5$H$_3$]zirconium dichloride (**3a**). Photolysis of **3a** with Pyrex-filtered UV/vis light at ambient temperature led to a rapid intramolecular [2+2]-cycloaddition reaction to yield a 1:1 mixture of the *meso-* and *rac*-isomers of the corresponding singly cyclobutylene-bridged *ansa*-metallocene system **4a**. Photolysis of this mixture with quartz-filtered UV light at −80 °C very slowly converted *meso*-**4a** to *rac*-**4a**. Over 2 days a 12:1 ratio of *rac/meso*-**4a** was achieved under these conditions.

Introduction

Carrying out functional group conversions at the sensitive group 4 bent metallocene framework is difficult.[1,2] A small series of suitable reactions have recently been worked out that can be compatible with the special features of zirconocene systems to allow for C−C coupling reactions at their frameworks to, for example, convert open, unbridged metallocenes to *ansa*-metallocenes.[3] These reactions include catalytic olefin metathesis,[4,5] the Mannich reaction,[6] and also a few examples of intramolecular photochemical [2+2]-cycloadditions.[7,8]

With selected examples we had previously shown that some substituted bis(alkenyl-Cp)ZrCl$_2$ systems (**1**) form the respective cyclobutylene-bridged *ansa*-metallocenes (**2**) upon photolysis. These reactions may be regarded as examples of a "dynamic topochemical reaction control".[7−10] In many cases photostationary equilibria were obtained upon irradiation with Pyrex-filtered light, which contained substantial amounts of the closed form (**2**).[7] We have now prepared a (1,3-dialkenylcyclopentadienyl)$_2$ZrCl$_2$ complex and subjected it to the photoinitiated C−C coupling reaction. This led to a number of interesting questions: would both pairs of alkenyl substituents be involved in photochemical carbon−carbon coupling to give a doubly bridged *ansa*-metallocene system? Would a *rac/meso*-mixture of the [2+2]-photocyclization product (**4**) be formed, or would one of the diastereoisomers be favored? Would the [2+2]-cycloaddition of **3** be reversible under our photochemical conditions? We tried to answer these and related questions by analyzing the photoproducts[11] derived from bis[1,3-di(1-methylethenyl)C$_5$H$_3$]zirconium dichloride (**3a**, R = CH$_3$).

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\# X-ray crystal structure analysis.

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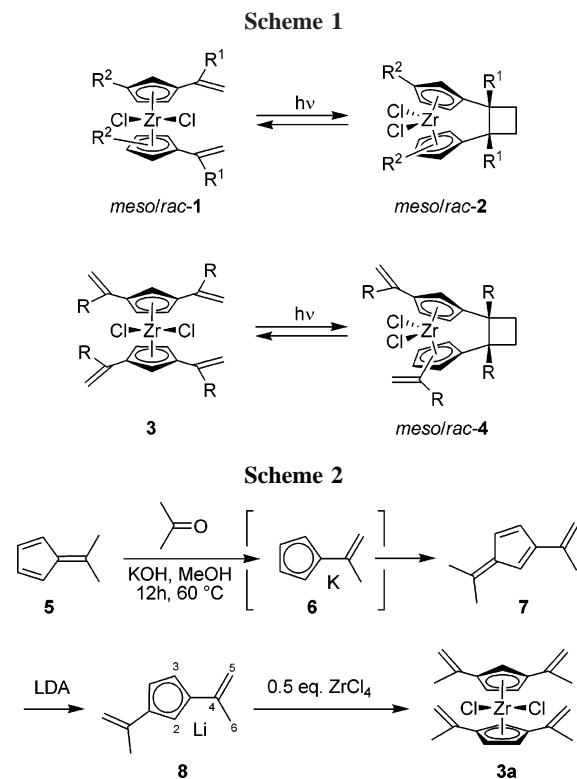
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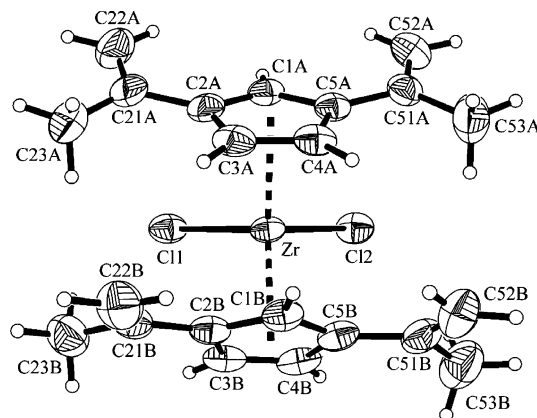
Scheme 1

Scheme 2

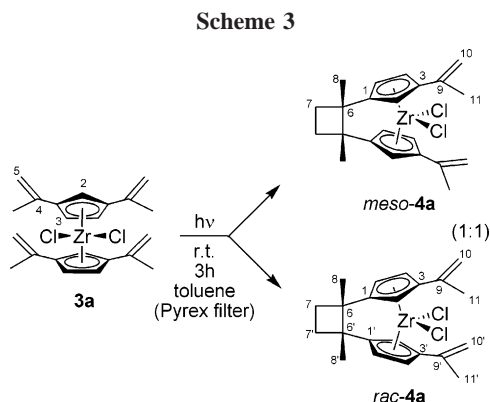**Figure 1.** Molecular structure of complex **3a** in the crystal.

functionalized zirconocene dichloride product as a bright yellow solid in 53% yield. At room temperature complex **3a** features NMR spectra of a conformationally equilibrated system [^{1}H NMR in toluene-d_8: δ 6.44 (2H)/5.86 (4H) (C$_5$H$_3$), 5.15/4.88 (8H, C=CH$_2$), 1.85 (s, 12H, CH$_3$); ^{13}C NMR: δ 130.2, 114.6, 111.6 (C$_5$H$_3$), 136.9, 112.5 (C=CH$_2$), 20.8 (CH$_3$)].

Complex **3a** was characterized by an X-ray crystal structure analysis. Suitable single crystals were obtained from a dichloromethane solution during 2 weeks at +4 °C. The structure of **3a** features a bent metallocene core [angles Cp(centroid)−Zr−Cp(centroid) 130.1°, Cl1−Zr−Cl2 97.76(2)°, bond lengths Zr−Cl1 2.432(1) Å, Zr−Cl2 2.436(1) Å] that bears four 1-methylethenyl substituents at its Cp rings. The ethenyl units are coplanar with the main planes of their adjacent Cp ring [dihedral angles C1A−C5A−C51A−C52A 8.3(3)°, C1B−C2B−C21B−C22B −7.5(3)°]. In each of the bis-1,3-(1-methylethenyl)C$_5$H$_3$ ligands the in-plane orientation is such that both the alkenyl groups are oriented toward the sector of the single C$_5$H$_3$ methine unit; that is, both C52A and C22A in ring A are *syn* with C1A, and C52B and C22B in ring B are *syn* arranged with C1B. The substituent C=C bonds are in the typical double-bond length range[16] (C21A−C22A 1.347(4) Å, C51A−C52A 1.326(3) Å, C21B−C22B 1.336(3) Å, C51B−C52B 1.357(4) Å), as are their bond angles (for details see the Supporting Information). The metallocene conformation[17] of complex **3a** in the crystal is staggered with a molecular symmetry close to C_s (but not crystallographically). This results in the substituent C=CH$_2$ double bonds of ring A becoming oriented toward the open front side of the bent metallocene wedge, whereas the C=CH$_2$ groups at ring B are facing toward the narrow metallocene backside. This orientation results in a small distortion of the bent metallocene core: the Zr−C3A (2.458(2) Å) and Zr−C4A (2.467(2) Å) bonds are slightly shorter than the remaining Zr−C(Cp) linkages, which are found in a narrow range between 2.515(2) Å (Zr−C1B) and 2.589(2) Å (Zr−C5A).

Photochemical *ansa*-Metallocene Synthesis. Photolysis of complex **3a** (HPK 125 Philips) with Pyrex-filtered light at ambient temperature for 3 h in toluene ($c \approx 0.06$ M) resulted in a quantitative conversion to a 1:1 mixture of two new organometallic products (*rac/meso*-**4a**, R = CH$_3$). After conventional workup the mixture was isolated in 90% yield. The NMR analysis (see below) has shown that each of the compounds (**4a**) still contained a pair of intact 1-methylethenyl

Results and Discussion

Synthesis and Characterization of the Starting Material. The synthesis of the [1,3-(1-methylethenyl)C$_5$H$_3$]$^-$ ligand system was carried out by a fulvene route.[12] For that purpose 6,6-dimethylfulvene (**5**)[13] was reacted with acetone under strongly basic conditions (KOH, MeOH, 12 h, 60 °C) analogously as previously described by Fenton et al.[14] to yield the (1-methylethenyl)-substituted pentafulvene derivative (**7**). This reaction is likely to proceed by deprotonation of the fulvene **5** to generate the (1-methylethenyl)cyclopentadienide (**6**), which under the reaction conditions is then trapped by acetone in a conventional pentafulvene synthesis to yield **7** (isolated in 37% to 50% yield). The fulvene **7** was then deprotonated by treatment with LDA[15] to yield the 1,3-bis(1-methylethenyl)cyclopentadienide reagent **8** (51% isolated, see Scheme 2). The reagent **8** was characterized spectroscopically [^{1}H NMR in THF-d_8: δ 6.11 (1H), 5.89 (2H, C$_5$H$_3$), 4.85, 4.25 ($^2J_{HH}$ = 3.3 Hz) (=CH$_2$), 1.99 (CH$_3$)] and then eventually subjected to the trans-metalation reaction to zirconium.

Treatment of the reagent **8** with ZrCl$_4$ in toluene followed by extraction with dichloromethane gave the tetra(alkenyl)-

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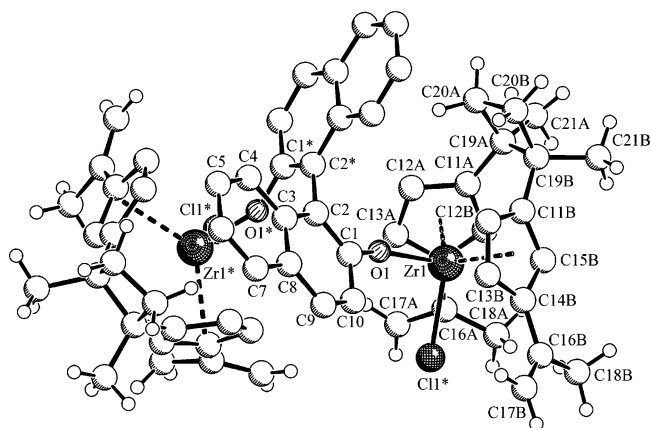
Scheme 3

Figure 2. View of the molecular structure of complex **10**. Some hydrogen atoms are omitted for clarity (only the *S*-enantiomer is depicted; see the Supporting Information for an ORTEP plot of **10**).

ligands. So only one pair each was utilized in the photochemical [2+2]-cycloaddition reaction. The NMR spectra also clearly revealed that both products were formed by head-to-head (i.e., symmetrical) cyclobutane ring formation and that the methyl groups at each four-membered ring were *cis*-oriented to each other. This left the possibility of the formation of a total of three diastereoisomeric products, namely, a *rac*- and two *meso*-forms ("*meso-syn*", "*meso-anti*"). Our experiment showed that only one of the *meso*-isomers was actually formed (*meso*-**4a**) along with the *rac*-[2+2]-cycloaddition product (*rac*-**4a**) (see Scheme 3).

Since we were not able to separate the two products, the complexes *rac*-**4a** and *meso*-**4a** were spectroscopically characterized from the mixture. *meso*-**4a** only features a single set of $^1H/^{13}C$ NMR resonances for the two halves of the molecule. It shows three sets of C_5H_3 ^1H NMR signals (δ 6.51, 6.00, 5.87). The alkenyl substituents show ^1H NMR signals at δ 5.31/5.06 (C=CH$_2$) and δ 2.02 (dd, ^4J = 1.5/0.8 Hz, CH$_3$). Most importantly, we monitored the typical NMR features of the newly formed cyclobutylene bridge of the *ansa*-metallocene *meso*-**4a**: methylene ^1H NMR signals at δ 2.13/1.54 (2H each) and the corresponding CH$_3$ signal at δ 0.95 (s, 6H). The ^{13}C NMR signals of the cyclobutylene moiety of complex *meso*-**4a** show up at δ 49.6 (C6), 30.2 (CH$_2$), and 24.6 (CH$_3$).

In contrast, the second component of the mixture, *rac*-**4a**, exhibits a "doubled" set of such characteristic NMR resonances due to its reduced molecular symmetry (C$_1$). As can be seen from the section of the ^1H NMR spectrum of *rac*-**4a** depicted in Figure 3 (see below), this chiral compound contains two inequivalent C_5H_3 rings [^1H NMR features at δ 6.67, 6.04, 5.58 (ring A), 6.50, 5.96, 5.89 (ring B)]. There are two inequivalent −C(CH$_3$)=CH$_2$ substituents [^1H NMR: δ 5.40/5.11 (=CH$_2^A$); 5.26/5.08 (=CH$_2^B$)]. The newly formed cyclobutylene bridge features a pair of methylene ^{13}C NMR signals [δ 30.7/30.0 (C7′/C7)] as well as a pair of quarternary carbon atoms adjacent to the Cp rings [δ 49.7/49.3 (C6/C6′)] and methyl groups at the four-membered carbocycle [δ 26.2/24.0 (C8/C8′)].

Unfortunately, we did not get single crystals of **4a** suitable for an X-ray crystal structure analysis of the ring-closed products; but we happened to obtain a few crystals of a derivative that supported the structural assignments. We mixed the starting material **3a** with the *rac*-1,1′-bi-2-naphtholato dilithium reagent (*rac*-**9**) in an NMR tube in dichloromethane-d_2. The ^1H NMR spectrum showed that under these conditions no immediate reaction occurred (Scheme 4). Subsequent photolysis of the sample apparently converted **3a** to the cyclobutylene-bridged *ansa*-metallocenes (*rac*-**4a**, *meso*-**4a**), which, being much more reactive than **3a**, reacted with the reagent **9**[18] to give a complicated mixture of products. After separation of the precipitated lithium chloride and slow evaporation of the

solvent a few single crystals were obtained that were suited for the characterization of a single component out of the complex product mixture by X-ray diffraction. The X-ray crystal structure analysis revealed the composition of the dinuclear binaphtholato-bridged bis-*ansa*-zirconocene **10**.

Although not being of particular importance in itself, the structure of the components of **10** illustrated the structural features of the cyclobutylene-bridged *ansa*-metallocenes that were formed upon photolysis of the bis[1,3-di(1-methylethenyl)-C$_5$H$_3$]ZrCl$_2$ starting material **3a**.

In the complex **10** one chloride ligand at the zirconium center has been replaced by a binaphtholato oxygen (Zr−O1 1.967(3) Å, angle Zr−O1−C1 151.4(2)°, Zr−Cl1 2.438(1) Å).[19] As a result, two of the photolytically formed cyclobutylene-bridged *ansa*-metallocene subunits were coupled by a bridging binaphtholato unit to make up the structure of the dinuclear complex **10**. The specific example isolated in the form of the racemic single crystals shows unique stereochemical features: both the involved *ansa*-metallocenes are *meso*-subunits, and they are connected by an *S*- or *R*-configured axially chiral binaphtholate atropisomer (C2−C2$^\#$ 1.494(7) Å, dihedral angle C1−C2−C2−C1$^\#$ 79.1(6)°) Thus, the structure of **10** provides some structural information about the framework (and its relative stereochemistry) of the obtained cyclobutylene-bridged *meso-ansa*-metallocene formed in the [2+2]-photocycloaddition of **3a**.

The *ansa*-zirconocene subunits in **10** are symmetry-equivalent. Each C$_5$H$_3$ ligand is η^5-coordinated to the metal with Zr−C(Cp) bond lengths ranging from 2.491(4) to 2.578(5) Å. Each Cp ring has a remaining −C(Me)=CH$_2$ substituent attached to it (C16A−C17A 1.373(10) Å, C16B−C17B 1.343(9) Å). The C=C double bonds of the alkenyl substituents are found arranged coplanar with their adjacent Cp rings [dihedral angles C13A−C14A−C16A−C17A 14.6(8)°, C13B−C14B−C16B−C17B −2.5(8)°], and a conformation is attained where the C=CH$_2$ unit points toward the open front side of the bent metallocene wedge.

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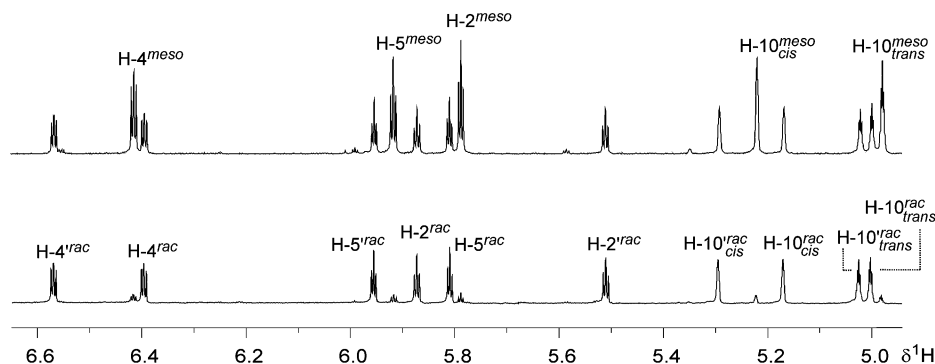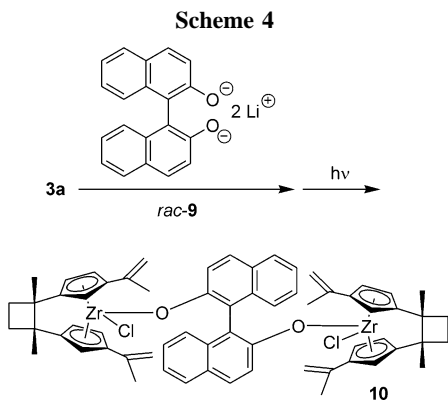
Figure 3. A section of the ^{1}H NMR spectra (500 MHz, toluene-d_8) of the 1:1 (top) and 12:1 *rac*-**4a**/*meso*-**4a** mixture (bottom), obtained after 2 h photolysis of **3a** (top) and after subsequent 2 day irradiation (quartz, −80 °C, bottom).

Scheme 4

The two pairs of Cp ligands in **10** are each linked by the newly formed dimethylcyclobutylene bridge. The structure of **10** confirms the head-to-head four-membered ring formation. The cyclobutane rings each bear a pair of methyl groups that are oriented *cis*, as consequently are the Cp rings attached to the cyclo-C$_4$ unit. The "internal" C−C bond length of the cyclobutylene ring is slightly elongated (C19A−C19B 1.546-(7) Å) as compared to the remaining distal (C20A−C20B 1.471-(10) Å) and lateral (C19A−C20A 1.534(7) Å, C19B−C20B 1.475(10) Å) cyclobutane carbon−carbon bonds in complex **10**. The sum of the internal C−C−C bonding angles of the cyclobutane ring is 358.4°. Both the proximal angles [C19B−C19A−C20A 86.9(4)°, C19A−C19B−C20B 89.5(5)°] are marginally smaller than the distal angles [C19A−C20A−C20B 90.1(5)°, C19B−C20B−C20A 91.9(5)°]. A static conformation is found where the cyclobutylene ring is oriented toward the lateral side of the bent metallocene wedge and the attached *cis*-pair of methyl groups faces the narrow backside (see Figure 2).

We were not able to separate *rac*-**4a** from *meso*-**4a**, but we were able to obtain close to pure *rac*-**4a** by a subsequent photolysis reaction under slightly altered reaction conditions. UV irradiation of the 1:1 *rac*/*meso*-**4a** mixture with quartz-filtered light in toluene solution at −80 °C for another 2 h had no measurable effect on the isomeric ratio. However, prolonged photolysis under these conditions slowly led to an isomerization of *meso*-**4a** to *rac*-**4a**. After 2 days a ca. 12:1 mixture of *rac*/*meso*-**4** was obtained (see Figure 3). Subsequent photolysis of this mixture with Pyrex-filtered light at ambient conditions did not lead to the formation of the original 1:1 mixture; the *rac*/*meso*-**4a** mixture of 12:1 remained unchanged. Prolonged photolysis at ambient temperature resulted in decomposition.

Conclusions

We assume that the initial [2+2]-photocyclization reaction, which leads to the formation of a 1:1 *rac*/*meso*-**4a** mixture,

Scheme 5
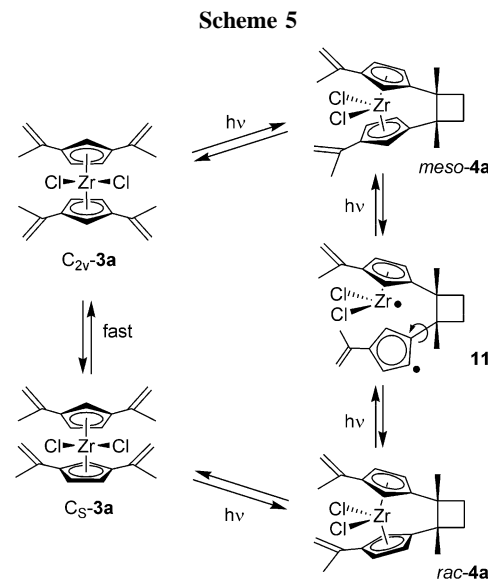
utilizes the rapid conformational equilibration[20] of the tetra-alkenyl-substituted metallocene **3a** to attain favorable relative orientations of the 1-methylethenyl substituents from which the dynamic topochemical reaction can either yield the *meso*-**4a** (from C_{2v}-**3a**) or the *rac*-**4a** isomer (from C_s-**3a**). The cyclobutane ring in **4a**, once it is formed, seems to be stable under the applied photochemical conditions and does not open easily. The slow subsequent *meso*-**4a** to *rac*-**4a** isomerization shows such pronouncedly different reaction characteristics that it very likely proceeds by a different mechanistic route (Scheme 5). In view of related photoinduced Cp-cleavage reactions of open group 4 metallocenes[21,22] and especially of related photochemical *meso*-

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to *rac-ansa*-metallocene interconversions[18] this subsequent photochemical *meso*-**4a** to *rac*-**4a** isomerization is likely to take place by a reaction sequence initiated by Zr−Cp homolysis (to reversibly generate the reactive intermediate **11**). Bond rotation at the stage of **11** followed by re-forming the Zr−Cp linkage would provide a plausible mechanistic explanation for this slow photochemical isomerization reaction. The **3a** ⇌ **4a** photostationary equilibrium under Pyrex irradiation at room temperature seems to be lying very far (or even exclusively) on the *ansa*-metallocene product side (**4a**). In combination with the slow subsequent *meso*-**4a** to *rac*-**4a** interconversion this seems to be another example to demonstrate the practical use of the [2+2]-photocycloaddition reaction at the bent metallocene state for the preparation of substituted or even functionalized group 4 *ansa*-metallocene systems.

Experimental Section

All reactions were carried out under Ar atmosphere employing a modified Schlenk and glovebox technique. NMR spectra were recorded on Varian 600 MHz unity plus, Varian INOVA 500 MHz, and Bruker AMX 400 MHz spectrometers with residual C_4D_7HO (3.58 ppm), $CDHCl_2$ (5.32 ppm), and $C_6D_5CD_2H$ (2.03 ppm) resonances as internal standard. 6,6-Dimethylfulvene (**5**) and (1-methylethenyl)-6,6-dimethylfulvene (**7**) were prepared according to published procedures.[13,14]

1,3-Di(1-methylethenyl)cyclopentadienyllithium (8). A solution of 20.0 g (137 mmol) of 6,6-dimethyl-3-(1-methylethenyl)fulvene (**7**) in 50 mL of ether was added dropwise to a solution of 14.7 g (137 mmol) of LDA in 150 mL of ether at 0 °C. After stirring for 4 h all volatiles were removed in vacuo. The resulting solid was suspended in pentane, collected by filtration, washed twice with 50 mL of pentane, and dried in vacuo to yield 10.5 g (69.3 mmol, 51%) of the white product **8**. ^{1}H NMR (400 MHz, THF-d_8): δ 6.11 (m, 1H, H-2), 5.89 (m, 2H, H-3), 4.85 (d ^2J = 3.3 Hz, 2H, H-5$_{cis}$), 4.25 (m, 2H, H-5$_{trans}$), 1.99 (s, 6H, H-6). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8): δ 142.9 (C-4), 122.9 (C-1), 103.7 (C-3), 101.3 (C-2), 99.6 (C-5), 23.0 (C-6).

Bis[1,3-di(1-methylethenyl)cyclopentadienyl]zirconium Dichloride (3a). To a mixture of 13.6 g (89.5 mmol) of **8** and 10.4 g (44.7 mmol) of zirconium tetrachloride was added 300 mL of precooled toluene at −78 °C. The suspension was stirred overnight and was allowed to come to ambient temperature. All volatiles were removed in vacuo, and the residue was extracted with 200 mL of dichloromethane in a Soxhlet apparatus for 12 h. The filtrate was reduced to half of its volume and stored at −30 °C. Overnight a yellow solid precipitated, which was collected by filtration. After washing with small amounts of pentane the product was dried in vacuo (yield of **3a**: 10.8 g, 53%). After keeping a concentrated solution of **3a** in dichloromethane for two weeks at +4 °C, crystals were obtained that were suitable for the X-ray crystal structure analysis: mp 140 °C; decomp 228 °C; λ_{max} (CH_2Cl_2, nm) 239 (ϵ = 26 600 ± 800 cm^2 mmol^{-1}), 387 (ϵ = 2160 ± 60 cm^2 mmol^{-1}). ^{1}H NMR (400 MHz, toluene-d_8): δ 6.44 (m, 2H, H-2), 5.86 (m, 4H, H-3), 5.15 (m, 4H, H-5$_{cis}$), 4.88 (m, 4H, H-5$_{trans}$), 1.85 (s, 12H, H-6). ^{13}C{^{1}H} NMR (100 MHz, toluene-d_8): δ 136.9 (C-4), 130.2 (C-1), 114.6 (C-2), 112.5 (C-5), 111.6 (C-3), 20.8 (C-6). IR (KBr): 3089(m), 2971(m), 2947(m), 2918(m), 1792(w), 1700(w), 1627(s), 1559(w), 1506(m), 1451(m), 1435(m), 1376(m), 1277-(w), 1170(w), 1066(m), 1003(w), 950(w), 893(vs), 855 (vs), 812-(s), 737(w), 622(w), 483(w), 448(w) cm^{-1}. Anal. Calcd for $C_{22}H_{26}ZrCl_2$: C, 58.39; H, 5.79. Found: C, 58.23; H, 6.13.

X-ray crystal structure analysis of **3a**: formula $C_{22}H_{26}Cl_2Zr$, M = 452.55, yellow crystal 0.35 × 0.20 × 0.10 mm, a = 11.920(1) Å, b = 13.579(1) Å, c = 13.236(1) Å, β = 101.85(1)°, V = 2096.7-(3) Å^3, ρ_{calc} = 1.434 g cm^{-3}, μ = 0.781 mm^{-1}, empirical absorption correction (0.772 ≤ T ≤ 0.926), Z = 4, monoclinic, space group

$P2_1/n$ (No. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 13 848 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.66 Å^{-1}, 4962 independent (R_{int} = 0.030) and 4159 observed reflections [$I \geq 2$ $\sigma(I)$], 230 refined parameters, R = 0.031, wR_2 = 0.083, max. residual electron density 0.47 (−0.53) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Data sets for **3a** and **10** (see below) were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction Denzo (Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Crystallogr.* **2003**, *A59*, 228−234), structure solution SHELXS-97 (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (Sheldrick, G. M. Universität Göttingen, 1997), graphics XP (BrukerAXS, 2000) and SCHAKAL (Keller, E., Universität Freiburg, 1997).

***rac/meso*-[1,2-Dimethylcyclobutylenebis(3-(1-methylethenyl)-cyclopentadienyl)]zirconium Dichloride (4a).** A solution of 4.07 g (8.99 mmol) of **3a** in 150 mL of toluene was irradiated with Pyrex-filtered UV light (HPK 125 Philips) at room temperature for 3 h. After filtration through a plug of Celite the volume was concentrated in vacuo (ca. 70 mL) and stored at −30 °C overnight. The precipitate was collected by filtration, washed twice with 10 mL of pentane each, and dried in vacuo. The product (**4a**) was isolated in 90% yield (3.65 g) as a 1:1 mixture of the *rac/meso*-diastereomers (only one of the two possible *meso*-diastereomers was observed): mp 213 °C; λ_{max} (CH_2Cl_2, nm) 238 (ϵ = 22 100 ± 700 cm^2 mmol^{-1}), ~261 (br shoulder, ϵ = 15 400 ± 500 cm^2 mmol^{-1}), 368 (ϵ = 1730 ± 50 cm^2 mmol^{-1}). NMR spectroscopic data of *meso*-**4a**: ^{1}H NMR (500 MHz, benzene-d_6): δ 6.51 (m, 2H, H-4), 6.00 (m, 2H, H-5), 5.87 (m, 2H, H-2), 5.31 (m, 2H, H-10$_{cis}$), 5.06 (pq, 2H, H-10$_{trans}$), 2.13 (m, 2H, H-7$_{cis}$), 2.02 (dd, J = 1.5 Hz, J = 0.8 Hz, 6H, H-11), 1.54 (m, 2H, H-7$_{trans}$), 0.95 (s, 6H, H-8). ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6): δ 141.6 (C-1), 137.1 (C-9), 136.2 (C-3), 117.7 (C-4), 113.6 (C-10), 108.5 (C-5), 105.2 (C-2), 49.6 (C-6), 30.2 (C-7), 24.6 (C-8), 21.4 (C-11). NMR spectroscopic data of *rac*-**4a**: ^{1}H NMR (500 MHz, benzene-d_6): δ 6.67 (m, 1H, H-4′), 6.50 (m, 1H, H-4), 6.04 (m, 1H, H-2′), 5.96 (m, 1H, H-5), 5.89 (m, 1H, H-2), 5.58 (m, 1H, H-5′), 5.40 (m, 1H, H-10′$_{cis}$), 5.26 (m, 1H, 10$_{cis}$), 5.11 (pq, 1H, H-10′$_{trans}$), 5.08 (pq, 1H, H-10$_{trans}$), 2.15, 2.00 (m, 2H, H-7$_{cis}$, H-7′$_{cis}$), 2.08 (dd, J = 1.6 Hz, J = 0.8 Hz, 3H, H-11′), 1.98 (dd, J = 1.6 Hz, J = 0.8 Hz, 3H, H-11), 1.58, 1.53 (m, 2H, H-7$_{trans}$, H-7′$_{trans}$), 0.99 (s, 6H, H-8, H-8′). ^{13}C{^{1}H} NMR (125 MHz, benzene-d_6): δ 142.7 (C-1′), 141.2 (C-1), 138.9 (C-3), 137.3 (C-9), 136.7 (C-9′), 132.0 (C-3′), 121.7 (C-4′), 115.4 (C-4), 113.6 (C-10, C-10′), 110.2 (C-5), 107.0 (C-2′), 106.0 (C-5′), 103.0 (C-2), 49.7 (C-6), 49.3 (C-6′), 30.7 (C-7′), 30.0 (C-7), 26.2 (C-8), 24.0 (C-8′), 21.4 (C-11′), 21.3 (C-11). IR (KBr): 3085(m), 2947(m), 2866(m), 1772(w), 1700(w), 1632(w), 1559(w), 1541 (w), 1450(w), 1450(m), 1373(m), 1257(m), 1238-(m), 1159(w), 1100(w), 1061(m), 1004(w), 939(w), 885(vs), 845-(vs), 816(s), 802(s), 737(m), 690(m), 669(w), 517(w) cm^{-1}. Anal. Calcd for $C_{22}H_{26}Zr$ Cl$_2$: C, 58.39; H, 5.79. Found: C, 58.46; H, 5.97.

Photochemical Isomerization of *rac/meso*-4a (1:1 ratio) to *rac/ meso*-4a (12:1). A quartz NMR tube, filled with a solution of 20 mg of **4a** in toluene-d_8, was irradiated with UV light (quartz filter, THF as cooling bath) at −80 °C for 2 days. The photochemical isomerization was monitored by ^{1}H NMR spectroscopy. The diastereomeric ratios were calculated from the integrals of the appropriate vinyl resonances (for *rac*-**4a** (600 MHz, toluene-d_8): δ 5.31 (pq, 6.31H, H-10′$_{cis}$), 5.19 (pq, 6.32H, H-10$_{cis}$); for *meso*-**4a** (600 MHz, toluene-d_8): δ 5.24 (pq, 1.00H, H-10$_{cis}$)).

Bis[1,2-dimethylcyclobutylenebis(3-(1-methylethenyl)cyclo-pentadienyl)]zirconium Chloride μ-1,1′-Bi-2-naphtholate (10). Dichloromethane-d_2 (0.5 mL) was added to a mixture of 30 mg

(0.07 mmol) of **3a** and 9.9 mg (0.03 mg) of dilithium *rac*-1,1′-bi-2-naphtholate (**9**). Irradiation with Pyrex-filtered UV light for 20 min at room temperature gave a complex product mixture. Lithium chloride was filtered off. Slow evaporation of the solvent furnished crystals of **10** that were suitable for the X-ray crystal structure analysis.

X-ray crystal structure analysis of **10**: formula $C_{64}H_{64}Cl_2O_2Zr_2$, $M = 1118.49$, yellow crystal $0.35 \times 0.30 \times 0.10$ mm, $a = 12.264$-(1) Å, $b = 16.982(1)$ Å, $c = 25.395(1)$ Å, $V = 5288.9(6)$ Å^3, $\rho_{calc} = 1.405$ g cm^{-3}, $\rho = 0.540$ cm^{-1}, empirical absorption correction ($0.834 \leq T \leq 0.948$), $Z = 4$, orthorhombic, space group *Pccn* (No. 56), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 39 547 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.67 Å^{-1}, 6518 independent ($R_{int} = 0.061$) and 3767 observed reflections [$I \geq 2\ \sigma(I)$], 316 refined parameters, $R = 0.057$, $wR_2 = 0.161$, max. residual electron density 0.67 (-0.57) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Supporting Information Available: Detailed experimental data, selected NMR spectra, and details of the X-ray crystal structure determination are available. This material is available free of charge via the Internet from http://pubs.acs.org.

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