Synthesis of *ansa*-Metallocenes by Intramolecular Photochemical [2 + 2] Cycloaddition of Bis(alkenylcyclopentadienyl)zirconium Complexes

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Reaction of the (alkenylcyclopentadienyl)lithium reagents $[C_5H_4C(R){=}CH_2]Li$ (**2a–c**, R = cyclohexyl, phenyl, or *o*-tolyl) with $ZrCl_4(THF)_2$ gave the metallocene complexes $[C_5H_4C(R){=}CH_2]_2ZrCl_2$ (**3a–c**). Complex **3c** was characterized by X-ray diffraction. It crystallizes in space group *Cm* with cell parameters $a = 6.802(1)$ Å, $b = 28.105(2)$ Å, $c = 6.860(1)$ Å, $\beta = 114.5(1)°$, $R = 0.023$, and $R_w = 0.030$. The reaction of the (1-alkenyl-3-alkylcyclopentadienyl)lithium reagents $[(C_5H_3R^1)C(R^2){=}CH_2]Li$ (**2d–f**, R^1 = isopropyl, R^2 = phenyl or cyclohexyl and R^1 = methyl, R^2 = cyclohexyl) gave the metallocene complexes $[(C_5H_3R^1)C(R^2){=}CH_2]_2ZrCl_2$ (**3d–f**). In each case a near to equimolar mixture of the respective rac and meso diastereoisomers was obtained. For **3d,e** these were separated by fractional crystallization. *rac*-Bis[η-1-(1-phenylethenyl)-3-isopropylcyclopentadienyl]zirconium dichloride (*rac*-**3d**) was characterized by X-ray diffraction. It crystallizes in space group *Pccn* with cell parameters $a = 22.122(1)$ Å, $b = 15.594(1)$ Å, $c = 16.576(1)$ Å, $R = 0.045$, and $R_w = 0.049$. With the exception of **3c**, these $(alkenyl{-}Cp)_2ZrCl_2$ complexes **3** undergo rapid intramolecular [2 + 2] cycloaddition upon photolysis. The photostationary equilibrium reached is dependent on the substituent pattern of the starting materials and the wavelength of the light employed. Near to quantitative conversion to the novel cyclobutene-bridged *ansa*-metallocene complexes **11** is achieved when alkyl substituents are used and the irradiation is carried out at 450 nm. The photochemically induced coupling of readily introduced alkenyl functionalities represents a useful synthetic pathway to novel C_2-hydrocarbyl-bridged *ansa*-metallocene systems of the early transition metals.

ansa-Metallocenes of the group 4 transition metals are of great importance as components of homogeneous Ziegler catalysts for the production of α-olefin polymers.[1] In addition, they find some use as stoichiometric reagents in asymmetric reactions involving metal-activated reagents.[2] Especially important are the *ansa*-metallocenes containing small bridges between the cyclopentadienyl (or indenyl) rings. Their high rigidity allows for very effective transfer of stereochemical information and often leads to thermally very stable catalyst systems or organometallic reagents.

The ansa bridges in group 4 transition metal chemistry are usually prepared at a rather early stage of the overall synthetic scheme. Usually, the Cp anion equivalents are coupled (as nucleophiles) with a suitable electrophilic derivative containing the chosen bridging system as an activated fragment. Sometimes, radical coupling or related reactions have also been used.[3] The reactive electrophilic transition metal center is then usually introduced at a late stage of the synthetic sequence. Very different from the metallocenes of the late transition metals, functional group chemistry at the early transition metal bent metallocene complexes is near to nonexistent, which is probably due to the high oxophilicity and reactivity of the electrophilic metal centers in these complexes.[4] The many successful syntheses of *ansa*-metallocene complexes show that this disadvantage of synthetic group 4 metallocene chemistry can be circumvented by practical means quite successfully. However, the need to construct all the necessary details

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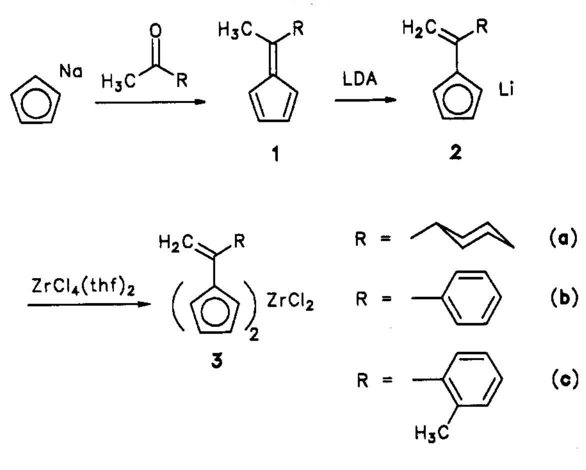
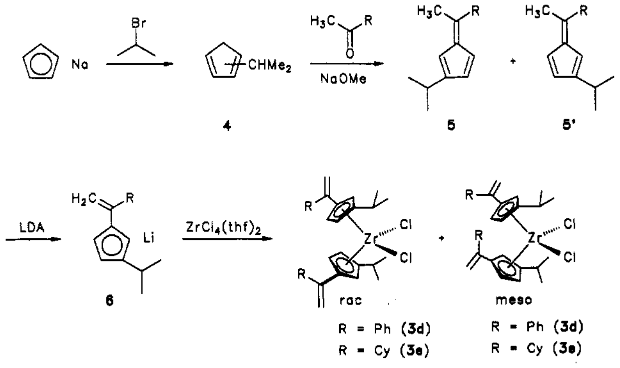
Scheme I



Scheme II



of a bridged *ansa*-Cp ligand system prior to its attachment to the early transition metal center is a conceptual weakness of synthetic group 4 metallocene chemistry that ought to be overcome by developing sets of reactions serving the anticipated synthetic purpose which are compatible with the special prerequisites of these reactive and sensitive early transition metal products.

We have recently shown that reactions at the olefin functionalities of readily available bis(alkenylcyclopentadienyl)ZrCl$_2$ complexes can often be carried out rather easily.[5] The conceptual similarity of the alkenyl–Cp moiety with the (neutral) alkenylarenes, which often undergo photochemically induced [2 + 2] cycloaddition reactions,[6] prompted us to investigate the possibility of forming cyclobutene-bridged group 4 *ansa*-metallocene complexes by irradiating zirconocene dihalide complexes having alkenyl units attached to their pairs of cyclopentadienyl ligand systems. In a number of cases this has led to the formation of the respective *ansa*-metallocene complexes.[7] A series of typical examples is reported in this article.

Results and Discussion

Preparation of the Bis(alkenylcyclopentadienyl)-ZrCl$_2$ Starting Materials. For this study we have employed six bis(alkenylcyclopentadienyl)zirconium dichlorides as substrates for the irradiation experiments. These metallocene complexes can be attributed to two subgroups which differ in their substitution pattern at the Cp ring systems. Within each subgroup simple substituent variation led to the specific complexes looked at.

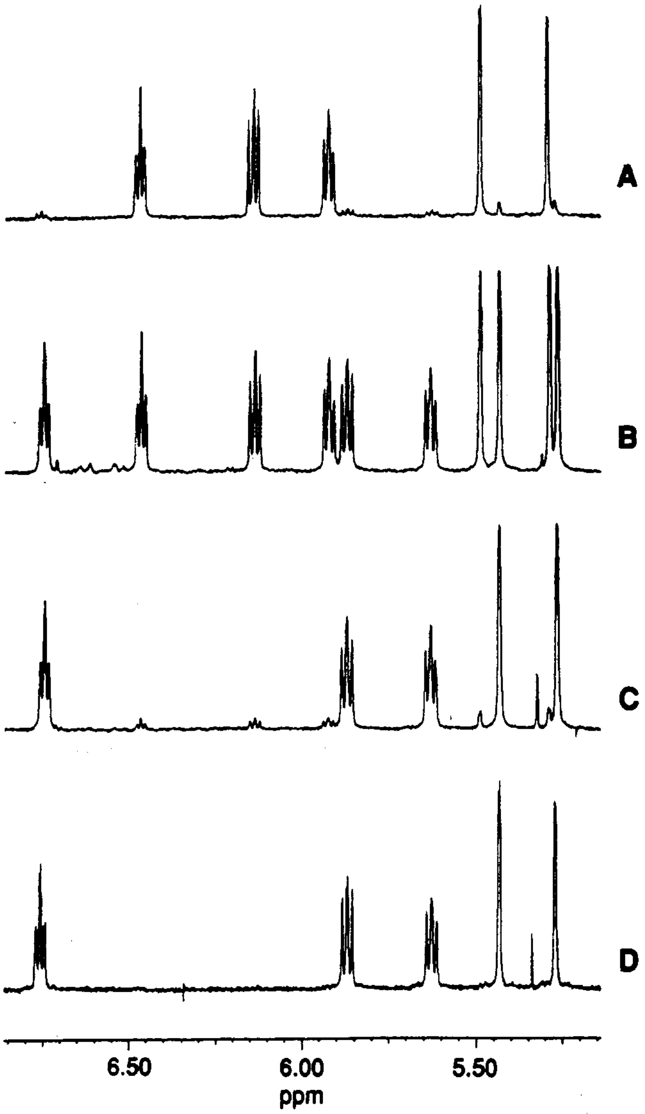


Figure 1. Separation of *meso*- and *rac*-**3d**. ^{1}H NMR spectra—$C_5H_3R(CPh{=}CH_2)$ region—of the pure isomers (spectra A and D), of the crude reaction product (B), and of the residue from the pentane extraction (C) are shown.

The first type of metallocene dihalides prepared (three examples) contain a simple $-(R)C{=}CH_2$ group at each Cp ring. The synthesis of such complexes is carried out straightforwardly starting from the respective fulvenes (see Scheme I), as previously described.[5,8] Thus, deprotonation of the suitably substituted 6-methylfulvenes (**1**, R = cyclohexyl (**a**), phenyl (**b**), or *o*-tolyl (**c**)) yields the (alkenylcyclopentadienyl)lithium systems **2**. Their reaction with 0.5 molar equiv of ZrCl$_4$(THF)$_2$ cleanly produced the (alkenyl-Cp)$_2$ZrCl$_2$ systems **3a–c** in high yield (e.g. complex **3c** (R = *o*-tolyl) was isolated analytically pure in ca. 90% yield).

Three additional substituted bis(alkenylcyclopentadienyl)zirconium dihalides were prepared whose compositions were slightly more complicated because of the introduction of disubstituted Cp ligands which led to the

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(7) Erker, G.; Wilker, S.; Krüger, C.; Goddard, R. *J. Am. Chem. Soc.* **1992**, *114*, 10983.

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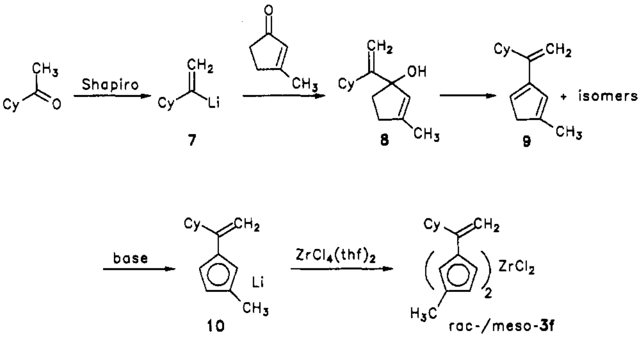
Scheme III



occurrence of two planar chirality elements per individual metallocene complex.[9] This combination of stereochemical features resulted in the formation of the respective pairs of meso and rac diastereomers.[10] In all three cases looked at, a mixture of the respective diastereoisomers was actually formed. In two systems these were readily separated by fractional crystallization. Only with the third example did we encounter difficulties in separating these stereoisomers. The photolysis experiments (see below) were in this single case, therefore, carried out with the diastereomeric mixture.

Two of these syntheses were carried out via variations of the fulvene route described above. We converted isopropylcyclopentadiene[11] (thermodynamic mixture of all isomers) by reaction with acetophenone to the fulvenes **5** and **5′** (54:46 mixture). Deprotonation with LDA gave the 3-isopropyl-substituted alkenyllithium reagent **6**[12] which was then reacted with 0.5 molar equiv of $ZrCl_4(THF)_2$ to yield >80% of a ca. 1:1 mixture of the *rac*-**3d** and *meso*-**3d** metallocene complexes.

The diastereomers *rac*- and *meso*-**3d** were separated by extraction of the crude reaction mixture with pentane followed by fractional crystallization from dichloromethane. As can be seen from the ^1H NMR spectra of the respective mixtures and fractions depicted in Figure 1 (only the ^1H NMR resonances of the Cp and alkenyl hydrogen atoms are shown), a single extraction with pentane resulted in a >95% diastereomeric separation.

The analogous cyclohexyl-substituted system **3e** was prepared accordingly. The mixture of diastereoisomers (*meso-/rac*-**3e** ≈ 1:1 directly obtained from the reaction) exhibits a solubility behavior similar to that observed for the *rac-/meso*-**3d** pair: simple pentane extraction led to a substantial isomeric enrichment (≥90% of each of the diastereomers). The pure meso and rac diastereoisomers were then obtained pure after repeated subsequent fractional crystallization from dichloromethane.

The bis[3-methyl(1-cyclohexylethenyl)cyclopentadienyl]-$ZrCl_2$ diastereomers (*rac-/meso*-**3f**) were prepared by a slightly different route because the attempted fulvene formation via methylcyclopentadiene was not of a sufficiently high regioselectivity. We, therefore, converted methyl cyclohexyl ketone to the alkenyllithium reagent **7** by means of a variant of the Shapiro reaction.[13] Subsequent addition to 3-methyl-2-cyclopentenone gave **8** selectively,[14] which was then converted to the 1,3-disubstituted cyclopentadiene **9** (mixture of the three conjugated diene isomers). Deprotonation furnished the (1-alkenyl-3-methylcyclopentadienyl)lithium reagent **10** which was then reacted with 0.5 molar equiv of $ZrCl_4(THF)_2$ to give the expected mixture of the metallocene *rac-/meso*-**3f** diastereomers. In contrast to the above described related systems we have not been successful in separating the *rac-/meso*-**3f** pair and thus employed it as such in the subsequent photolysis reactions (see below).

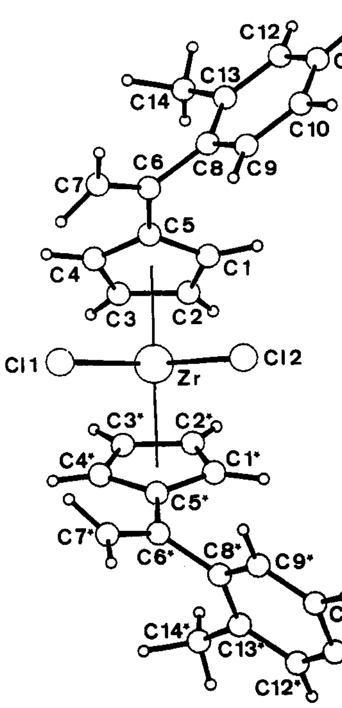


Figure 2. Molecular structure of complex **3c**.

X-ray Crystal Structure Analyses. The bis[(1-cyclohexylethenyl)cyclopentadienyl]zirconium complex **3a** was previously characterized by X-ray diffraction and described.[5] For this study we have in addition obtained crystals of the complexes **3c** and *rac*-**3d** which were suited for X-ray crystal structure determinations.

Single crystals of bis[(1-*o*-tolylethenyl)cyclopentadienyl]zirconium dichloride (**3c**) were obtained from dichloromethane. In the crystal complex **3c** is C_s-symmetric. The alkenyl substituents at the Cp rings of the bent metallocene unit are both oriented toward the open front side of the bent metallocene wedge. Of the frequently observed rotational orientations of $(RCp)_2MX_2$

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Table I. Selected Bond Lengths (Å), Angles, and Dihedral Angles (deg) of 3c

Zr–Cl(1)	2.442(1)	Zr–Cl(2)	2.440(1)
Zr–C(1)	2.529(2)	Zr–C(2)	2.462(3)
Zr–C(3)	2.470(2)	Zr–C(4)	2.531(2)
Zr–C(5)	2.586(1)	C(1)–C(2)	1.401(4)
C(1)–C(5)	1.414(4)	C(2)–C(3)	1.395(6)
C(3)–C(4)	1.406(4)	C(4)–C(5)	1.406(4)
C(5)–C(6)	1.484(3)	C(6)–C(7)	1.333(4)
C(6)–C(8)	1.490(2)		
Cl(2)–Zr–Cl(1)	96.5(1)	C(5)–C(1)–C(2)	108.5(3)
C(3)–C(2)–C(1)	107.7(3)	C(4)–C(3)–C(2)	108.6(2)
C(5)–C(4)–C(3)	107.9(3)	C(6)–C(5)–C(4)	127.7(2)
C(6)–C(5)–C(1)	124.8(2)	C(4)–C(5)–C(1)	107.2(2)
C(8)–C(6)–C(7)	120.5(2)	C(8)–C(6)–C(5)	116.7(2)
C(7)–C(6)–C(5)	122.7(2)		
C(1)–C(5)–C(6)–C(7)	–159.1		
C(4)–C(5)–C(6)–C(7)	28.6		
C(5)–C(6)–C(8)–C(9)	–122.2		
C(7)–C(6)–C(8)–C(9)	60.3		

Table II. Positional Parameters of 3c

atom	*x*	*y*	*z*
Zr	0.0000	0.0000	0.0000
Cl(1)	0.3045(1)	0.0000	–0.1011(1)
Cl(2)	–0.2829(1)	0.0000	–0.3636(1)
C(1)	–0.1848(4)	0.0771(1)	0.0152(4)
C(2)	–0.1217(8)	0.0536(1)	0.2117(6)
C(3)	0.1033(8)	0.0539(1)	0.3110(4)
C(4)	0.1816(5)	0.0768(1)	0.1754(3)
C(5)	0.0029(5)	0.0920(1)	–0.0082(5)
C(6)	0.0037(3)	0.1226(1)	–0.1840(3)
C(7)	0.1698(4)	0.1243(1)	–0.2392(6)
C(8)	–0.1884(3)	0.1536(1)	–0.2928(3)
C(9)	–0.3082(4)	0.1495(1)	–0.5136(3)
C(10)	–0.4855(4)	0.1783(1)	–0.6222(4)
C(11)	–0.5464(3)	0.2114(1)	–0.5106(5)
C(12)	–0.4282(4)	0.2165(1)	–0.2927(4)
C(13)	–0.2489(3)	0.1882(1)	–0.1796(3)
C(14)	–0.1207(5)	0.1968(1)	0.0546(4)

bent metallocene complexes **3c** belongs to the conformational type characterized by a bis-central:syn arrangement of groups at the metallocene framework.[15,16] The $-(Ar)C{=}CH_2$ alkenyl group is rotated by 28.6° [C(4)—C(5)—C(6)—C(7)] relative to the plane of the adjacent Cp ring, with both 1,1-disubstituted olefin groups pointing toward the same side. The bulky *o*-tolyl substituents are substantially rotated away from conjugation [dihedral angle C(7)—C(6)—C(8)—C(9) = 60.3°]. The metal—halogen bond lengths are in the typical range at Zr—Cl(1) = 2.442(1) and Zr—Cl(2) = 2.440(1) Å.[17] The Cl(1)—Zr—Cl(2) angle in **3c** is 96.5(1)° (cf.: Cp_2ZrCl_2, Zr—Cl = 2.44 Å and angle Cl—Zr—Cl 97.2°;[18] $(Me_3CCp)_2ZrCl_2$, Zr—Cl = 2.457 Å and angle Cl—Zr—Cl 94.2°). In **3c** the angle between the Cp ring planes is 60.5° [e.g., as compared to the typical 51.4° observed for $(Me_3CCp)_2ZrCl_2$ and related compounds[16,19]].

The bis[1-(1-phenylethenyl)-3-isopropylcyclopentadienyl]zirconium dichloride complex *rac*-**3d** shows similar overall structural features but a distinctly different conformational preference than **3c**. In the crystal the Zr–Cl(1) and Zr–Cl(2) distances are 2.432(1) and 2.434(1) Å, respectively. The Cl(1)–Zr–Cl(2) angle is 98.3(1)°. The angle between the planes of the Cp ring systems in *rac*-**3d** is slightly smaller at 56.1° than that found in **3c**.

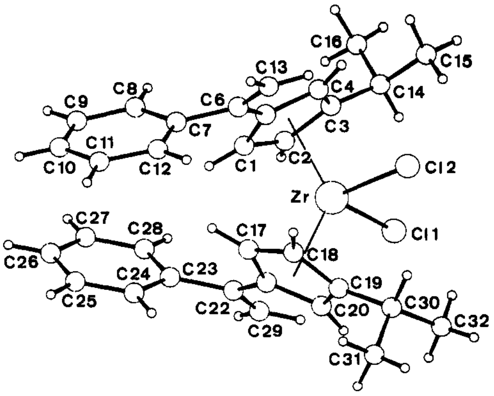

Figure 3. View of the molecular structure of *rac*-**3d**.

In *rac*-**3d** the alkenyl groups do not deviate much from coplanarity with the Cp rings. The corresponding dihedral angles are found at -15.5° [C(4)–C(5)–C(6)–C(13)] and -15.6° [C(20)–C(21)–C(22)–C(29)], respectively. Both phenyl substituents are rotated markedly away from this plane [dihedral angles C(13)–C(6)–C(7)–C(12) -41.3°, C(29)–C(22)–C(23)–C(28) -42.9°].

Complex *rac*-**3d** exhibits a metallocene conformation which is nearly C_2 symmetric and has the 1-phenylethenyl substituents oriented toward the lateral sectors of the bent metallocene unit [the dihedral angle C(5)–D(1)–D(2)–C(21) is 239.6° (D(1) and D(2) denote the centroids of the cyclopentadienyl rings)]. In this arrangement the alkenyl carbon vectors C(6)–C(13) and C(22)–C(29) are directed away from the center of the bent metallocene, while the phenyl substituents attached at C(6) and C(22), respectively, are oriented toward the narrow back part of the bent metallocene wedge. This overall conformation allows the bulky isopropyl substituents to be arranged in the front sector in a staggered conformational orientation.

Projections as depicted in Figure 4 show the marked conformational differences of the $(alkenyl–Cp)_2ZrCl_2$ complexes **3a**, **3c**, and *rac*-**3d**. The characteristic differ-

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Table III. Selected Bond Lengths (Å) and Angles (deg) of *rac*-3d

Zr–Cl(1)	2.432(1)	Zr–Cl(2)	2.434(1)
Zr–C(1)	2.481(3)	Zr–C(2)	2.507(3)
Zr–C(3)	2.585(3)	Zr–C(4)	2.556(2)
Zr–C(5)	2.500(2)	Zr–C(17)	2.490(3)
Zr–C(18)	2.507(3)	Zr–C(19)	2.575(3)
Zr–C(20)	2.545(3)	Zr–C(21)	2.502(3)
Zr–H(14)	3.625	Zr–H(30)	3.716
C(1)–C(2)	1.407(4)	C(1)–C(5)	1.426(4)
C(2)–C(3)	1.418(4)	C(3)–C(4)	1.406(4)
C(3)–C(14)	1.500(4)	C(4)–C(5)	1.417(4)
C(5)–C(6)	1.490(4)	C(6)–C(7)	1.478(4)
C(6)–C(13)	1.330(4)	C(14)–C(15)	1.493(5)
C(14)–C(16)	1.512(5)	C(17)–C(18)	1.409(4)
C(17)–C(21)	1.427(4)	C(18)–C(19)	1.415(4)
C(19)–C(20)	1.405(4)	C(19)–C(30)	1.508(4)
C(20)–C(21)	1.416(4)	C(21)–C(22)	1.491(4)
C(22)–C(23)	1.487(4)	C(22)–C(29)	1.324(4)
C(30)–C(31)	1.514(5)	C(30)–C(32)	1.510(5)

Cl(2)–Zr–Cl(1)	98.3(1)	C(5)–C(1)–C(2)	108.1(2)
C(3)–C(2)–C(1)	109.1(2)	C(14)–C(3)–C(4)	126.8(2)
C(14)–C(3)–C(2)	126.6(2)	C(4)–C(3)–C(2)	106.4(2)
C(5)–C(4)–C(3)	110.1(2)	C(6)–C(5)–C(4)	125.7(2)
C(6)–C(5)–C(1)	128.0(2)	C(4)–C(5)–C(1)	106.3(2)
C(13)–C(6)–C(7)	120.8(3)	C(13)–C(6)–C(5)	120.6(3)
C(7)–C(6)–C(5)	118.5(2)	C(16)–C(14)–C(15)	110.1(3)
C(16)–C(14)–C(3)	109.8(3)	C(15)–C(14)–C(3)	113.7(3)
C(21)–C(17)–C(18)	107.8(2)	C(19)–C(18)–C(17)	109.2(2)
C(30)–C(19)–C(20)	127.5(2)	C(30)–C(19)–C(18)	125.9(2)
C(20)–C(19)–C(18)	106.4(2)	C(21)–C(20)–C(19)	110.1(2)
C(22)–C(21)–C(20)	126.4(2)	C(22)–C(21)–C(17)	127.2(2)
C(20)–C(21)–C(17)	106.4(2)	C(29)–C(22)–C(23)	120.4(3)
C(29)–C(22)–C(21)	121.1(3)	C(23)–C(22)–C(21)	118.5(2)
C(32)–C(30)–C(31)	110.9(3)	C(32)–C(30)–C(19)	113.7(3)
C(31)–C(30)–C(19)	108.6(3)		

Table IV. Positional Parameters of *rac*-3d

atom	*x*	*y*	*z*
Zr	0.3446(1)	0.0069(1)	0.1902(1)
Cl(1)	0.4088(1)	0.1066(1)	0.1169(1)
Cl(2)	0.4236(1)	–0.0764(1)	0.2555(1)
C(1)	0.2541(1)	0.0751(2)	0.2511(1)
C(2)	0.2964(1)	0.1417(2)	0.2416(2)
C(3)	0.3450(1)	0.1286(2)	0.2959(1)
C(4)	0.3324(1)	0.0521(2)	0.3374(1)
C(5)	0.2768(1)	0.0172(2)	0.3105(1)
C(6)	0.2484(1)	–0.0631(2)	0.3408(1)
C(7)	0.1837(1)	–0.0782(2)	0.3236(2)
C(8)	0.1415(1)	–0.0131(2)	0.3292(2)
C(9)	0.0807(2)	–0.0288(3)	0.3143(2)
C(10)	0.0622(2)	–0.1103(4)	0.2946(2)
C(11)	0.1031(2)	–0.1748(3)	0.2888(2)
C(12)	0.1641(2)	–0.1600(2)	0.3029(2)
C(13)	0.2803(1)	–0.1193(2)	0.3836(2)
C(14)	0.3967(1)	0.1888(2)	0.3112(2)
C(15)	0.4455(2)	0.1513(2)	0.3624(2)
C(16)	0.3735(2)	0.2708(2)	0.3486(3)
C(17)	0.2570(1)	–0.0746(2)	0.1349(1)
C(18)	0.3037(1)	–0.1351(2)	0.1446(2)
C(19)	0.3502(1)	–0.1176(2)	0.0884(2)
C(20)	0.3320(1)	–0.0444(2)	0.0454(1)
C(21)	0.2749(1)	–0.0161(2)	0.0732(1)
C(22)	0.2406(1)	0.0597(2)	0.0443(1)
C(23)	0.1750(1)	0.0655(2)	0.0620(2)
C(24)	0.1372(1)	–0.0059(2)	0.0563(2)
C(25)	0.0760(2)	0.0007(2)	0.0715(2)
C(26)	0.0512(2)	0.0779(3)	0.0942(2)
C(27)	0.0881(2)	0.1490(3)	0.1003(2)
C(28)	0.1490(2)	0.1427(2)	0.0842(2)
C(29)	0.2671(1)	0.1196(2)	–0.0007(2)
C(30)	0.4049(2)	–0.1728(2)	0.0730(2)
C(31)	0.3859(2)	–0.2491(2)	0.0227(3)
C(32)	0.4566(2)	–0.1254(3)	0.0334(2)

Table V. Details of the Data Collection and Structure Solution of 3c[a] and *rac*-3d[b]

	3c	*rac*-3d
mol formula	$C_{28}H_{26}Cl_2Zr$	$C_{32}H_{34}Cl_2Zr$
mol wt	524.6	580.8
cryst color	green yellow	yellow
cryst syst	monoclinic	orthorhombic
space group (no.)	*Cm* (8)	*Pccn* (56)
a, Å	6.802(1)	22.122(1)
b, Å	25.105(2)	15.594(1)
c, Å	6.860(1)	16.576(1)
β, deg	114.45(1)	
V, Å^3	1193.8	5718.4
Z	2	8
D_{calcd}, g cm^{-3}	1.46	1.35
μ, cm^{-1}	6.91	5.84
Kα radiation, λ, Å	0.710 69	0.710 69
F(000), e	536	2400
diffractometer	Enraf-Nonius CAD4	
scan mode	$\omega-2\theta$	$\omega-2\theta$
$[(\sin\theta)/\lambda]_{max}$, Å^{-1}	0.74	0.70
T, °C	20	20
no. of measd rflns	4260 ($\pm h,\pm k,+l$)	9188 ($+h,+k,+l$)
no. of indep rflns	3918	8317
no. of obsd rflns ($I > 2\sigma(I)$)	3906	5720
no. of refined params	195	316
R	0.023	0.045
R_w ($w = 1/\sigma^2(F_o)$)	0.030	0.049
resid electron dens, e Å^{-3}	0.52	0.43
structure solution	heavy-atom method	heavy-atom method

[a] The H atom positions were found and included in the final refinement stages. [b] The H atom positions were calculated and kept fixed in the final refinement stages.

ences of the relative orientation of the alkenyl functional groups become very clear in these top views. The observed preferred conformers in these complexes place the two alkenyl functional groups at very different positions with regard to their potential intramolecular interaction (the chemical consequences resulting from such an induced alkenyl/alkenyl interaction will be described below). At the front sector of the bent metallocene wedge, the Cp-conjugated alkenyl substituents are at their utmost vertical (i.e. projected normal to the σ-ligand plane) spatial separation. This situation—which is, e.g., extremely unfavorable for any intramolecular alkenyl–alkenyl coupling—is found for complex **3c** in the solid state.

In **3a** the Cp-bound alkenyl moieties are still far away from each other, but they have moved (by Cp rotation) already almost half the way toward the narrow back part of the bent metallocene. The respective conformational dihedral angle characterizing this situation is 143.2° [C(1)–D–D′–C(1′)]. In *rac*-**3d** this "rotation" is even further advanced. The alkenyl moieties bound to Cp have moved further to the bent metallocene backside. At θ = 239.6° [C(5)–D(1)–D(2)–C(21)] both olefin substituents are clearly occupying part of the rear sector at the $(RCp)_2M$ backbone. Their induced interaction would require only another few degrees in metallocene rotation in addition to some conformational reorientation at the substituent itself. We have indeed observed that for some of the bis(alkenyl–Cp)$ZrCl_2$ complexes looked at in this study, including the structurally characterized examples **3c** and *rac*-**3d**, intramolecular coupling of the olefin side chains can be achieved.

Photochemical Coupling Reactions. The bis(alkenylcyclopentadienyl)zirconium dichloride complexes **3** were photolyzed in dilute solution in separate experiments at two wavelengths. One set of experiments was carried out employing a high-pressure mercury lamp Philips HPK 125/Pyrex filter (300–350 nm maximum, see Table VI). Additional experiments were carried out using a Rayonet photolysis reactor with a 450-nm lamp set.

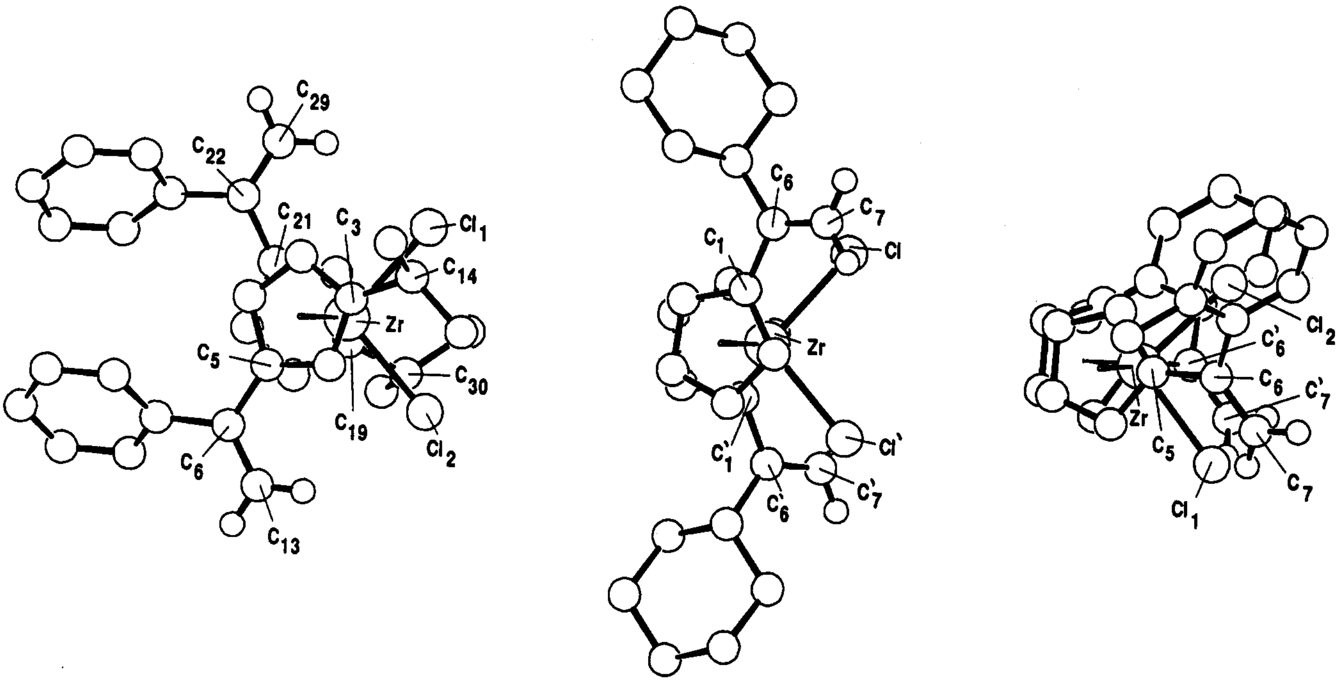


Figure 4. Comparison of the metallocene conformations of complexes *rac*-**3d** (left), **3a** (center), and **3c** (right) as observed in the crystal by X-ray diffraction (SCHAKAL plots).

Table VI. Intramolecular [2 + 2] Photocyclization of Bis(alkenylcyclopentadienyl)zirconium Dichlorides $[R^1C_5H_3C(R^2){=}CH_2]_2ZrCl_2$ (3)

R^1	R^2	starting material	product	photostationary equilibrium reached[a] 300–350 nm[b]	450 nm[c]
H	cyclohexyl	**3a**	**11a**	70	>98
H	phenyl	**3b**	**11b**	15	*d*
H	*o*-tolyl	**3c**	**11c**	*d*	*e*
isopropyl	phenyl	*rac*-**3d**	*rac*-**11d**	5	53
		meso-**3d**	*meso*-**11d**	37	79
			meso-**11d′**	7	8
isopropyl	cyclohexyl	*rac*-**3e**	*rac*-**11e**	75	>98
		meso-**3e**	*meso*-**11e**	90	>98
methyl	cyclohexyl	*rac*-**3f**	*rac*-**11f**	*e*	90[f]
		meso-**3f**	*meso*-**11f**		

[a] Percent product (**11**) is given, the remaining material is educt. [b] HPK 125, Pyrex filter. [c] Rayonett reactor. [d] No product formation observed. [e] Not tested. [f] The *rac*-/*meso*-**3f** mixture (1:1) was photolyzed.

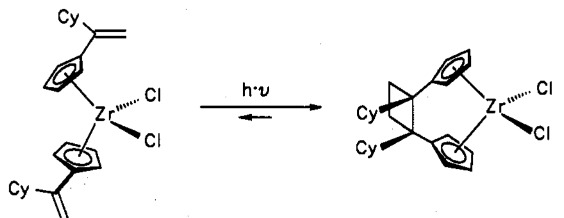
Table VII. UV/Vis Absorptions of the $(Alkenyl–C_5H_3R)_2ZrCl_2$ Complexes 3 and Their Photocyclization Products 11

starting material	λ_{max}[a] (ϵ)	product	λ_{max}[a] (ϵ)
3a	246 (139 000), 333 (1200), 364 (1300)	**11a**	238 (117 000)
rac-**3d**	233 (131 000), 336 (4200), 378 (4200)	*rac*-**11d**	*b*
meso-**3d**	224 (150 000), 331 (6300)	*meso*-**11d**	238 (54 000)
rac-**3e**	239 (22 200), 374 (4090)	*rac*-**11e**	234 (56 100)
meso-**3e**	242 (20 400), 369 (3030)	*meso*-**11e**	240 (49 000)

[a] nm, in CH_2Cl_2 ($c \approx$ 0.01–0.04 mmol/L). [b] Not determined.

Irradiation of bis[1-(1-cyclohexylethenyl)cyclopentadienyl]zirconium dichloride (**3a**) in benzene-d_6 solution at 300–350 nm rapidly resulted in the formation of a new product. After 4 h of photolysis a 70:30 product/starting material mixture was obtained which did not change upon further irradiation at these wavelengths. In a separate experiment, a sample of **3a** dissolved in benzene-d_6 was irradiated with 450-nm light. Within 1 h this led to an almost complete conversion to the new product (>98%). Subsequent photolysis of this solution with light from the 300–350-nm light source rapidly reestablished the 70:30 photostationary equilibrium achieved in our first experiment (for the UV/vis spectral data of the product/starting material pair of isomers see Table VII).

Complex **3a** was then photolyzed on a preparative scale in toluene solution at 450 nm. The reaction was complete after ca. 3 h. The photoproduct was isolated (55%) and identified as the cyclobutene-bridged *ansa*-metallocene complex **11a**.[20] A single isomer of the *ansa*-metallocene complex was formed and isolated. According to its spectroscopic data (see Table IX and Experimental Section) and by analogy to the photocyclization products obtained from the *rac*-/*meso*-(alkenyl–$C_5H_3R)_2ZrCl_2$ complexes (see below) we have assigned this product (**11a**) a C_s-symmetric structure, exhibiting the cyclohexyl substituents in a cis orientation at adjacent carbon centers at the cyclobutane moiety which was newly formed by head-to-head coupling in this intramolecular photoreaction.[6]



3a (Cy = cyclohexyl) 11a

The 1-arylethenyl-substituted metallocene complexes **3b** and **3c** turned out to be unsuitable starting materials

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[20] For examples of remotely related organometallic [2 + 2] cycloaddition reactions see: Nakanishi, K.; Mizuno, K.; Otsuji, Y. *J. Chem. Soc., Perkin Trans. 1* **1990**, 3362. Nakadira, Y.; Sakurai, H. *Tetrahedron Lett.* **1971**, 1183. Bichler, R. E. J.; Booth, M. R.; Clark, H. C. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 71. See also: Nesmeyanov, A. N.; Sazonova, V. A.; Romanenko, V. I.; Rodionova, N. A.; Zolnikova, G. P. *Dokl. Akad. Nauk. SSSR* **1963**, *149*, 1354; *Chem. Abstr.* **1963**, *59*, 3460. Related reviews: Bozak, R. E. *Adv. Photochem.* **1971**, *8*, 227. Seebach, D. In *Houben-Weyl, Methoden der Organischen Chemie*; Müller, E., Ed.; Thieme, Stuttgart, 1971; Vol. IV/4. Kaupp, G., *Ibid.* 1975, Vol. IV/5a; pp 278–412.

Table VIII. Selected $^1H/^{13}C$ NMR Data for Diastereomeric Pairs of Bis(alkenylcyclopentadienyl)zirconium Dichloride Complexes 3[a]

	^{13}C NMR							^1H NMR				
compd	C(1)/C(3)		C(2)/C(4)/C(5)			$-C(R)=CH_2$		H(2)/H(4)/H(5)			$=CH_2$	
rac-**3d**	123.1	141.3	120.7	115.3	112.8	142.3	109.5	6.75	5.87	5.65	5.40	5.23
meso-**3d**	119.5	141.8	116.2	115.9	112.7	142.2	111.3	6.42	6.10	5.88	5.46	5.26
rac-**3e**	127.3	141.1	117.8	112.7	108.6	147.5	109.7	6.46	6.11	5.65	5.27	5.06
meso-**3e**	130.2	142.1	113.9	111.6	109.8	147.1	109.6	6.35	6.12	5.89	5.30	5.07
rac-**3f**	129.4	130.0	116.3	115.3	110.1	147.8	109.6	6.23	6.13	5.74	5.27	4.99
meso-**3f**	128.9	129.6	119.2	115.5	112.4	147.5	109.6	6.37	6.05	5.64	5.27	4.99

[a] NMR spectra in $CDCl_3$, except **3f** (benzene-d_6). Chemical shifts relative to TMS, δ scale.

Table IX. Selected $^1H/^{13}C$ NMR Data for the Cyclobutene-Bridged *ansa*-Metallocene Complexes 11[a]

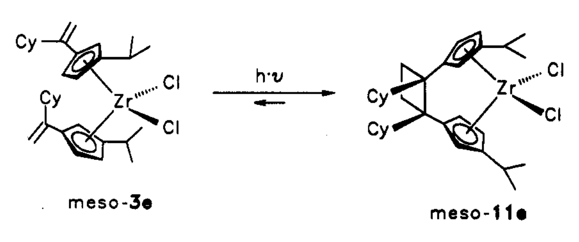
					^{13}C NMR						
compd	^1H NMR Cp hydrogens				C1/C3	C(2)/C(4)/C(5)				cyclobutene C	
11a	6.71	6.22	5.97	5.72	129.0	127.1	116.3	114.2	107.4	59.9	31.1
11b	6.62	6.33	6.17	5.64							
rac-**11d**	6.60	6.39	6.35		145.9[b]/142.3	115.3	114.0	113.6		60.3[b]	33.2[b]
	6.21	6.04	5.81		138.2	112.8	109.5	106.8			
meso-**11d**	6.32[b]	5.77			146.6/138.9	115.6	112.8	107.9		60.7	33.3
meso-**11d'**	6.61	6.11	5.86								
rac-**11e**	6.63	6.15	6.01		149.0[b]/141.4	115.0	112.9	111.6		60.0[b]	33.7
	5.89[b]	5.85			138.7	108.7	106.2	104.7			33.5
meso-**11e**	6.12	6.07	5.87		148.7/138.4	115.7	112.0	104.9		60.0	33.1

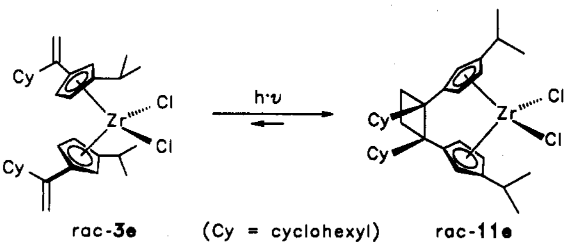
[a] NMR spectra in benzene-d_6, chemical shifts relative to TMS, δ scale. [b] Double intensity.

for the photochemical conversion to the cyclobutene-bridged *ansa*-metallocenes under the experimental conditions applied for this study. Upon 300–350-nm irradiation we observed about 15% conversion of **3b** to **11b**. Surprisingly, 450-nm photolysis did not result in appreciable product formation. In the case of the 1-(*o*-tolyl)ethenyl-substituted analogue **3c** we did not observe any [2 + 2] cycloaddition product formation at all.

The situation is much more favorable when the complexes containing suitably 1,3-disubstituted cyclopentadienyl ligand systems are employed. The photochemistry of the bis[1-(1-cyclohexylethenyl)-3-isopropylcyclopentadienyl]$ZrCl_2$ system **3e** is very typical for this situation. Photolysis of the pure *meso*-**3e** system with 300–350-nm light in toluene solution rapidly results in the formation of *meso*-**11e** (90% composition in the photostationary equilibrium reached at this wavelength).

Irradiation of *meso*-**3e** at 450 nm leads to a quantitative conversion to the 1,2-dicyclohexylcyclobutene-bridged *ansa*-metallocene *meso*-**11e**. Complex *meso*-**11e** was isolated and characterized spectroscopically (see Table IX).



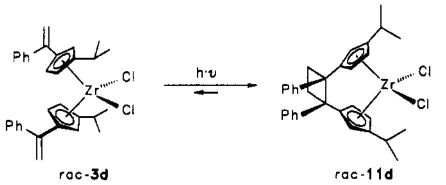


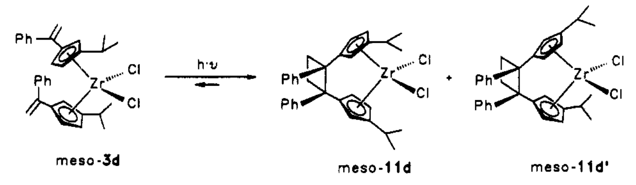
In addition, in this case it was independently confirmed by an X-ray crystal structure analysis that product formation had exclusively taken place by photochemically induced intramolecular syn, head-to-head [2 + 2] cycloaddition yielding the C_s-symmetric *cis*-1,2-dicyclohexylcyclobutene-bridged *ansa*-metallocene *meso*-**11e**.[7]

The photochemistry of the isomeric complex *rac*-**3e** proceeds similarly. In this case, the 300–350-nm irradiation in toluene solution results in a photostationary equilibrium mixture containing 75% of the [2 + 2] cycloaddition product *rac*-**11e**. Photolysis with 450-nm light again leads to a complete conversion of the alkenyl-substituted metallocene system (*rac*-**3e**) to a single *ansa*-metallocene isomer (*rac*-**11e**). Complex *rac*-**11e** exhibits NMR spectra as expected for an asymmetric product (C_1).

This independently confirms that only syn-oriented head-to-head [2 + 2] cycloaddition has taken place[21] and that the relative assignment of the respective bis(alkenyl-Cp)$ZrCl_2$ diastereomers as *rac*-**3** and *meso*-**3** was correct (see Tables VIII and IX).

Again [2 + 2] photocyclization of the phenyl-substituted analogous system (**3d**) is more difficult. Photolysis of *rac*-**3d** in benzene solution at 300–350 nm rapidly reaches a photostationary equilibrium that contains only about 5% of the anticipated *ansa*-metallocene product *rac*-**11d**. In contrast to **3b** and **3c** (see above) the situation is here markedly improved when 450-nm irradiation is employed.





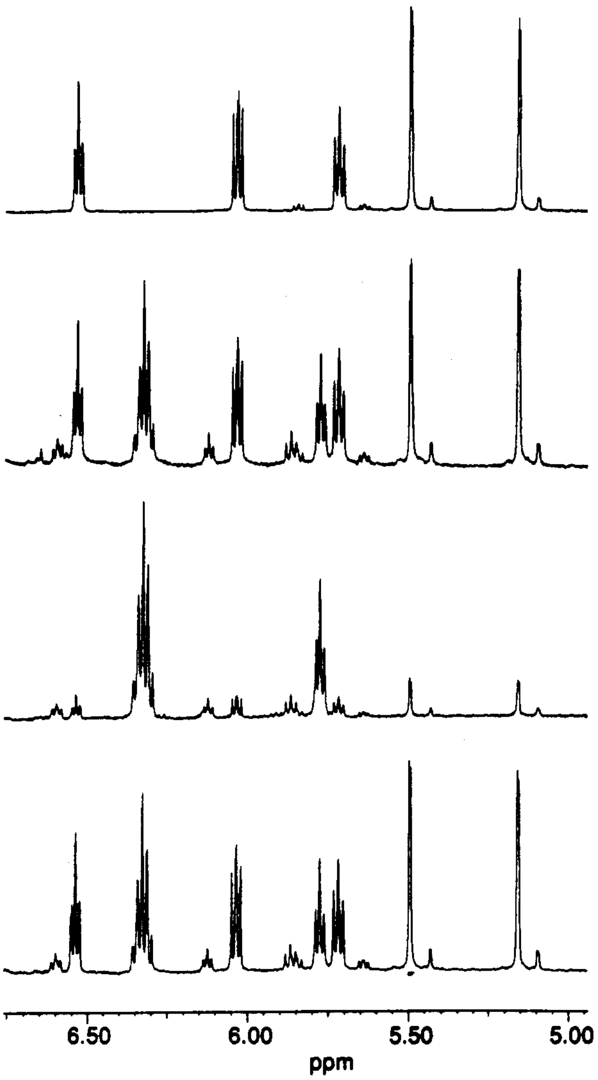


Figure 5. Photostationary equilibria of *meso*-**3d**, *meso*-**11d**, and *meso*-**11d′** at 300–350 nm (spectra B and D) and 450 nm (spectrum C). For details of this experiment see text.

In this case a conversion of *rac*-**3d** to *rac*-**11d** of up to 53% could be achieved. The situation is even more favorable when the achiral bis(alkenyl–C_5H_3R)$ZrCl_2$ isomer *meso*-**3d** is employed. Photolysis at 300–350 nm yields from almost 40% *meso*-**11d** at equilibrium. This proportion can even be increased to almost 80% upon irradiation at 450 nm. In each case, a second minor isomer of the photoproduct was observed (see Table VI). We assign to this the structure of the other possible C_s-symmetric syn, head-to-head [2 + 2] cycloaddition product (*meso*-**11d′**). In a separate experiment we have confirmed that both products *meso*-**11d** and *meso*-**11d′** are participating in the photostationary equilibration with the starting material *meso*-**3d**. For this purpose we have dissolved the ≥96% pure *meso*-**3d** diastereomer in benzene-d_6 and photolyzed it at 300–350 nm. The ^{1}H NMR spectrum (Cp and olefin region) of the resulting 56:37:7 mixture of *meso*-**3d**, *meso*-**11d**, and *meso*-**11d′** is depicted in Figure 5 (spectrum B). Further irradiation at 450 nm then resulted in the formation of a mixture containing the three metallocene complexes *meso*-**3d**, **11d**, and **11d′** in a 13:79:8 ratio (Figure 5, spectrum C). Subsequent photolysis of this very mixture again with our 300–350-nm light source rapidly reestablished the previously observed photostationary equilibrium mixture at *meso*-**3d**:-**11d**:-**11d′** = 56:37:7 (Figure 5, spectrum D).

Conclusions

Our study shows that alkenyl substituents attached to the η-cyclopentadienyl ligands of group 4 bent metallocenes can serve as functional groups suited for making novel *ansa*-metallocene complexes. We have shown that the alkenyl functionalities which are conjugated with the cyclopentadienyl π-system can be used for photochemical coupling reactions. [2 + 2] cycloaddition takes place readily upon electronic excitation. It has turned out that the reverse of this useful *ansa*-metallocene formation takes place equally facilely after suitable photochemical activation. As usual, the wavelength-dependent photostationary equilibrium reached can be partly controlled by substituents exerting an influence on the UV/vis absorption characteristics of starting materials and products. In our case, attaching aryl substituents at the system had an adverse effect on the photochemical *ansa*-metallocene formation due to its favorable influence on the [2 + 2] cycloreversion. The reversibility of the intramolecular photochemical *ansa*-metallocene formation becomes much less important when only substituents are employed that do not contribute to the UV/vis absorption of the product at longer wavelengths. In those cases almost complete conversion to the interesting novel *ansa*-metallocene systems can easily be achieved. Making use of these photochemical reaction characteristics should make a variety of similar *ansa*-metallocene systems synthetically available in high yield by a rather simple preparative sequence employing readily introduced alkenyl substituents as suitable functional groups at the cyclopentadienyl rings of rather sensitive metallocene systems.

Experimental Section

Reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or a glovebox. All solvents were dried and distilled under argon prior to use. The following spectrometers were used: Bruker WP 200 SY and AC 200 FT NMR spectrometers (200.1 MHz, ^{1}H; 50.3 MHz, ^{13}C); Nicolet 5-DXC FT IR spectrometer; Shimadzu UV 2100 UV/vis spectrometer. Melting points (SMP Gallenkamp, sealed capillaries) are uncorrected. Elemental analyses were carried out using a Foss-Heraeus CHN-Rapid elemental analyzer. Photolyses were carried out with either a high-pressure mercury lamp Philips HPK 125 using a Pyrex filter (300–350 nm maximum) or a Rayonet RPR 100 reactor with a 450-nm lamp set. The following compounds were prepared according to literature procedures: $ZrCl_4(THF)_2$,[22] isopropylcyclopentadiene (**4**),[11] bis[η-(1-cyclohexylethenyl)cyclopentadienyl]zirconium dichloride (**3a**),[5] and bis[η-(1-phenylethenyl)cyclopentadienyl]zirconium dichloride (**3b**).[5]

6-Methyl-6-(2-methylphenyl)fulvene (1c). A sodium methoxide solution was prepared from 4.3 g (186 mmol) of sodium and 100 mL of methanol. To this solution was added dropwise a mixture of 25.0 g (186 mmol) of methyl 2-methylphenyl ketone and 19.1 g (23.0 mL, 279 mmol) of freshly distilled cyclopentadiene. The reaction mixture was then kept at 45 °C with stirring for 6 h. Water was then added (100 mL) and the mixture extracted with three 75-mL portions of ether. The combined ethereal

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[21] Nishimura, J.; Obayashi, A.; Doi, H.; Nishimura, K. *Chem. Ber.* **1988**, *121*, 2019. Nishimura, J.; Horikoshi, Y.; Wada, Y.; Takahashi, H.; Machino, S.; Oku, A. *Tetrahedron Lett.* **1989**, *30*, 5439. Inokuma, S.; Yamamoto, T.; Nishimura, J. *Tetrahedron Lett.* **1990**, *31*, 97.

[22] Manzer, L. E.; Deaton, J.; Sharp, P.; Schrock, R. R. *Inorg. Synth.* **1982**, *21*, 135.

phases were washed with water and then with brine. Solvent was removed and the fulvene **1c** distilled twice in vacuo to give 10.3 g (30%) of **1c**, bp 110 °C (10^{-2} Torr). Anal. Calcd for $C_{14}H_{14}$ (182.3): C, 92.26; H, 7.74. Found: C, 92.31; H, 7.70. IR (film): ν 3069, 2924, 1636, 1487, 1362, 1038, 892, 767, 638 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.26–7.14 (m, 4H, arom), 6.66, 6.59, 6.40, 5.85 (m, 1H each, cyclopent), 2.46 (s, 3H, Ar–CH$_3$), 2.25 (s, 3H, COC*H*$_3$). ^{13}C NMR (CDCl$_3$, DEPT): δ 150.0 (C(6)), 144.4 (C(1)), 142.1, 134.6 (ipso-C, Ph), 132.0, 131.0, 129.9, 128.1 (arom C*H*), 127.5, 125.1, 123.3, 120.5 (cyclopent C*H*), 22.9, 19.7 (C*H*$_3$).

Formation of the Lithium Compound 2c. To a suspension of 3.5 g (32.8 mmol) of LDA in 50 mL of tetrahydrofuran was added dropwise a solution of 7.5 g (41.0 mmol) of the fulvene **3c** in 50 mL of ether at −40 °C. The reaction mixture was allowed to warm to ambient temperature and then stirred for 3 h. Volatiles were then removed in vacuo. Ether (50 mL) was added. The product (**2c**) precipitated. It was collected by filtration and dried to give 4.5 g (58%) of **2c**. ^{1}H NMR (benzene-d_6/tetrahydrofuran-d_8 4:1): δ 7.34 (m, 1H), 7.13–7.10 (m, 3H, arom), 6.10 (m, 4H, cyclopent), 5.57 (m, 1H) and 4.66 (m, 1H, =CH$_2$), 2.41 (s, 3H, CH$_3$). ^{13}C NMR (benzene-d_6/tetrahydrofuran-d_8 4:1, DEPT): δ 149.0 (*C*=CH$_2$), 146.3, 136.7 (ipso-C, Ph), 129.9, 129.5, 126.4, 125.0 (arom *C*H), 120.9 (ipso-C, Cp), 105.1, 104.3 (cyclopent *C*H), 101.0 (C=*C*H$_2$), 20.3 (*C*H$_3$).

Bis[η-[1-(2-methylphenyl)ethenyl]cyclopentadienyl]zirconium Dichloride (3c). A solution of 4.3 g (23 mmol) of [[1-(2-methylphenyl)ethenyl]cyclopentadienyl]lithium (**2c**) in 50 mL of tetrahydrofuran was added to a suspension of 4.3 g (11.5 mmol) of ZrCl$_4$(THF)$_2$ in 100 mL of toluene. The Schlenk tube was sealed, and the mixture was kept at 55 °C for 3 days. The solvent was then removed in vacuo. The residue was taken up in methylene chloride and filtered from the precipitated lithium chloride. From the filtrate the CH$_2$Cl$_2$ solvent was distilled in vacuo to give 5.4 g (90%) of **3c** which was ≥98% pure according to its ^{1}H NMR spectrum. Recrystallization (2×) from methylene chloride gave crystals suited for the X-ray crystal structure analysis (for details see Table V), mp 168 °C dec. Anal. Calcd for $C_{28}H_{26}Cl_2Zr$ (524.6): C, 64.10; H, 4.99. Found: C, 64.14; H, 4.86. IR (KBr): ν 2975, 1616 (C=C), 1379, 907, 772, 741 cm^{-1}. UV (CH$_2$Cl$_2$, c = 0.0285 mmol L^{-1}): λ_{max} 239 nm (ϵ 39 300), 348 (5300). ^{1}H NMR (CDCl$_3$): δ 7.19–7.14 (m, 8H, C$_6$*H*$_4$), 6.20 (m, 8H, cyclopent C*H*), 5.77, 5.22 (AX, ^3J = 1.0 Hz, 2H each, C=CH$_2$), 2.06 (s, 6H, CH$_3$). ^{13}C NMR (CDCl$_3$, DEPT): δ 141.1 (*C*=CH$_2$), 140.2, 135.7, (ipso-C, Ph), 130.0, 129.6, 127.7, 125.6 (arom *C*H), 128.1 (ipso-C, Cp), 117.1 (C=*C*H$_2$), 115.4, 114.3 (cyclopent *C*H), 19.7 (CH$_3$).

3-Isopropyl-6-methyl-6-phenylfulvene (5d, 5d′). A sodium methoxide solution was prepared by dissolving 3.5 g (150 mmol) of sodium metal in 60 mL of methanol. To this was added a solution of 25.0 g (30 mL, 230 mmol) of isopropylcyclopentadiene (**4**) and 18.4 g (18 mL, 150 mmol) of acetophenone in 30 mL of methanol. The reaction mixture was stirred for 4 days at room temperature. Water (100 mL) was added and the mixture extracted three times with a total volume of 500 mL of ether. The combined ethereal phases were washed with water and with brine and dried over sodium sulfate. Solvent was removed in vacuo and the residual product distilled to give 22.3 g (46%) of a 54:46 mixture of the fulvenes **5** and **5′**, bp 98–110 °C (10^{-2} Torr). Anal. Calcd for $C_{16}H_{18}$ (210.3): C, 91.37; H, 8.63. Found: C, 91.18; H, 9.34. IR (film): ν 2960, 2927, 1622, 1442, 1380, 1365, 909, 812, 764, 699 cm^{-1}. ^{1}H NMR (CDCl$_3$): first isomer δ 7.43–7.35 (m, 5H, Ph), 6.66, 6.58, 5.86 (m, each 1H, cyclopent C*H*), 2.71 (m, 1H) and 1.15 (d, ^3J = 6.8 Hz, 6H, isopropyl), 2.52 (s, 3H, CH$_3$); second isomer δ 7.43–7.35 (m, 5H, Ph), 6.47, 6.29, 6.19 (m, each 1H, cyclopent C*H*), 2.71 (m, 1H) and 1.24 (d, ^3J = 6.8 Hz, 6H, isopropyl), 2.53 (s, 3H, CH$_3$). An absolute assignment of the NMR signals belonging to the specific isomers **5d** and **5d′** was not achieved. ^{13}C NMR (CDCl$_3$, both isomers, DEPT): δ 154.9, 154.5 (C(6)), 143.2, 142.3, 142.2 (ipso-C, Ph and Cp), 132.5, 132.3, 124.6, 121.9, 115.6, 113.2 (cyclopent *C*H), 129.1, 127.9, 127.8 (Ph), 29.1, 28.9 (*C*HMe$_2$), 22.4 (CH$_3$), 22.3, 22.0 (CH(*C*H$_3$)$_2$).

Deprotonation of 3-Isopropyl-6-methyl-6-phenylfulvene. LDA (2.1 g, 19.2 mmol) was suspended in 50 mL of tetrahydrofuran. To this was added dropwise at −40 °C a solution of 4.8 g (4.8 mL, 23 mmol) of the **5d/5d′** mixture in 50 mL of ether. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. Volatiles were then removed in vacuo, and the lithium compound **6d** precipitated by adding 50 mL of ether. The isolated compound **6d** (2.6 g, 63%) was characterized spectroscopically. ^{1}H NMR (benzene-d_6/tetrahydrofuran-d_8 4:1): δ 7.63 (m, 2H) and 7.19–7.12 (m, 3H, Ph), 6.02, 5.93, 5.83 (m, 1H, each, cyclopent C*H*), 5.30 and 4.71 (AX, ^2J = 2.7 Hz, 2H, C=C*H*$_2$), 2.95 (sept, 1H) and 1.31 (d, ^3J = 6.8 Hz, 6H, isopropyl). ^{13}C NMR (benzene-d_6/tetrahydrofuran-d_8, DEPT): δ 149.7 (*C*=CH$_2$), 146.3 (ipso-C, Ph), 129.2, 127.6, 126.6 (Ph), 129.1, 118.5 (ipso-C, Cp), 104.0, 102.4, 101.8 (*C*H, Cp), 101.1 (C=*C*H$_2$), 29.3 (*C*HMe$_2$), 25.8 (CH(*C*H$_3$)$_2$).

Bis[η-1-(1-phenylethenyl)-3-isopropylcyclopentadienyl]zirconium Dichloride (3d). To a suspension of 2.3 g (6.05 mmol) of ZrCl$_4$(THF)$_2$ in 50 mL of toluene was added dropwise a solution of 2.6 g (12.1 mmol) of the lithium reagent **6d** in 50 mL of tetrahydrofuran. The yellow solution was then kept at 60 °C for 3 days with stirring. During this time some precipitate had formed. Solvent was removed from the reaction mixture in vacuo. The yellow residue was treated with 50 mL of methylene chloride and filtered. Solvent was removed in vacuo from the clear filtrate to yield 3.0 g (86%) of a crude mixture of the **3d** diastereoisomers. These were separated as follows. The yellow solid was stirred with pentane (50 mL) and filtered. The remaining solid consists of a 9:1 mixture of *rac*-**3d** and *meso*-**3d**. Repeated recrystallization from methylene chloride (4×) gave a 0.35-g sample of ≥99% pure *rac*-**3d**, mp 164 °C. This material was used for the X-ray crystal structure determination (for experimental details see Table V). The pentane-soluble fraction was recrystallized twice from pentane to yield 0.40 g of pure *meso*-**3d**. Anal. Calcd for $C_{32}H_{34}Cl_2Zr$ (580.8): C, 66.18; H, 5.90. Found: C, 66.10; H, 5.84. IR (KBr): ν 3098, 2962, 1607 (C=C), 1493, 1448, 1386, 1086, 890, 867, 812 cm^{-1}. *rac*-**3d**: ^{1}H NMR (CDCl$_3$) δ 7.37–7.24 (m, 10H, Ph), 6.75, 5.87, 5.65 (m, each 2H, cyclopent C*H*), 5.40, 5.23 (AX, ^2J = 1.1 Hz, 2H each, C=C*H*$_2$), 3.27 (m, 2H) and 1.38, 1.27 (d, each 6H, isopropyl); ^{13}C NMR (CDCl$_3$, DEPT) δ 142.3, 141.3, 140.3, 123.1 (*C*=CH$_2$, ipso-C Ph and Cp), 128.4, 128.1, 128.0 (Ph), 120.7, 115.3, 112.8 (cyclopent *C*H), 109.5 (C=*C*H$_2$), 28.7 (isopropyl *C*H), 24.8, 21.4 (isopropyl *C*H$_3$). *meso*-**3d**: ^{1}H NMR (CDCl$_3$) δ 7.33–7.22 (m, 10H, Ph), 6.42, 6.10, 5.88 (m, 2H each, cyclopent C*H*), 5.46, 5.26 (AX, ^2J = 1.1 Hz, 2H each, C=C*H*$_2$), 2.99 (m, 2H), 1.21, 1.17 (d, each 6H, isopropyl); ^{13}C NMR (CDCl$_3$, GATED) δ 142.2, 141.8, 140.5, 119.5 (*C*=CH$_2$, ipso-C Ph and Cp), 128.3, 128.0, 127.5 (Ph), 116.2, 115.9, 112.7 (cyclopent *C*H), 111.3 (C=*C*H$_2$), 28.2 (isopropyl *C*H), 23.6, 22.8 (isopropyl *C*H$_3$).

6-Cyclohexyl-3-isopropyl-6-methylfulvene (5e, 5e′). To a solution of 15.0 g (118 mmol, 13.8 mL) of cyclohexyl methyl ketone and 26.0 g (240 mmol, 31.3 mL) of isopropylcyclopentadiene in 75 mL of methanol was added dropwise a solution of 12.8 g (180 mmol, 14.7 mL) of pyrrolidine in 35 mL of methanol. The orange solution was stirred for 7 days at ambient temperature. The reaction was quenched by adding 10.6 mL of glacial acetic acid and then 40 mL of water. The mixture was extracted with three 50-mL portions of ether. The combined ether layers were washed with water (50 mL) and brine (50 mL) and then dried over sodium sulfate. Solvent was removed and the product distilled in vacuo to yield 12.9 g (50%) of a 40:60 mixture of **5e** and **5e′**, bp 105 °C (10^{-2} Torr). Anal. Calcd for $C_{16}H_{24}$ (216.4): C, 88.82; H, 11.18. Found: C, 89.24; H, 11.53. IR (film): ν 2929, 2853, 1630, 1448, 1379, 1369, 869, 809 cm^{-1}. Minor isomer: ^{1}H NMR (CDCl$_3$) δ 6.60–6.41 (m, 3H, cyclopent C*H*), 2.95–2.82 (m, 1H, cyclohexyl C*H*), 2.68 (sept, 1H, isopropyl C*H*), 2.09 (s, 3H, CH$_3$), 1.82–1.64, 1.51–1.23, 1.01–0.92 (m, 10H, cyclohexyl C*H*$_2$), 1.18 (d, ^3J = 6.9 Hz, 6H, isopropyl C*H*$_3$); ^{13}C NMR (CDCl$_3$, DEPT) δ 157.2, 153.1, 141.2 (*C*=*C*) (ipso-C cyclopent), 131.0, 120.5, 112.0 (cyclopent *C*H), 44.4 (cyclohexyl *C*H), 31.4, 26.3, 26.1 (cyclohexyl *C*H$_2$), 29.0 (isopropyl *C*H), 22.3 (isopropyl *C*H$_3$), 16.6 (*C*H$_3$). Major isomer: ^{1}H NMR (CDCl$_3$): δ 6.60–6.41 (m, cyclopent C*H*), 2.95–2.82 (m, cyclohexyl CH), 2.68 (sept, 1H, isopropyl CH), 2.08 (s, CH$_3$), 1.82–1.64, 1.51–1.23, 1.01–0.92 (m, 10H, cyclohexyl CH_2), 1.17 (d, 6H, isopropyl CH_3); ^{13}C NMR (CDCl$_3$, DEPT) δ 153.5, 153.1, 131.4 ($C{=}C$) (ipso-C cyclopent), 131.0, 121.8, 113.2 (cyclopent CH), 44.5 (cyclohexyl CH), 31.6, 26.3, 26.1 (cyclohexyl CH$_2$), 29.0 (isopropyl CH), 22.1 (isopropyl CH$_3$), 16.4 (CH$_3$).

Deprotonation of 6-Cyclohexyl-3-isopropyl-6-methylfulvene. LDA (2.0 g, 19.0 mmol) was suspended in 50 mL of tetrahydrofuran, and the mixture was cooled to −40 °C. To this was added dropwise a solution of 5.0 g (5.0 mL, 23 mmol) of the **5e**/**5e′** fulvene mixture in 40 mL of ether. The solution was decolorized instantaneously. The reaction mixture was allowed to warm to room temperature. All volatiles were then removed in vacuo. The lithium reagent **6e** was precipitated by adding 40 mL of ether. Filtration gave 3.3 g (65%) of **6e** which was characterized spectroscopically. ^{1}H NMR (benzene-d_6/tetrahydrofuran-d_8 4:1): δ 5.99 (m, 2H) and 5.74 (m, 1H, cyclopent CH), 5.09, 4.50 (AX, 1H each, C=CH_2), 2.92 (sept, ^{3}J = 6.8 Hz, 1H, isopropyl CH), 2.56 (m, 1H, cyclohexyl CH), 1.88–1.67, 1.42–1.02 (m, 10H, cyclohexyl CH_2), 1.30, 1.29 (d, 6H, isopropyl CH$_3$). ^{13}C NMR (benzene-d_6/tetrahydrofuran-d_8 4:1, DEPT): δ 153.6 (C=CH$_2$), 122.6, 119.8 (ipso-C Cp), 101.5, 100.7, 99.5 (cyclopent CH), 96.0 (C=CH$_2$), 43.2 (cyclohexyl CH), 34.7 (3-fold intensity), 27.9, 27.4, 26.5, 26.3 (cyclohexyl CH$_2$), 25.9, 25.7 (isopropyl CH), 21.4, 21.3 (isopropyl CH$_3$).

Bis[η-1-(1-cyclohexylethenyl)-3-isopropylcyclopentadienyl]zirconium Dichloride (3e). To a suspension of 2.8 g (7.4 mmol) of ZrCl$_4$(THF)$_2$ in 50 mL of toluene was added dropwise a solution of the lithium reagent **6e** (3.3 g, 14.8 mmol) in 35 mL of tetrahydrofuran. The mixture was then kept at 60 °C for 5 days with stirring. The volatiles were then removed in vacuo, and the residue was stirred with 50 mL of methylene chloride and filtered from the precipitated lithium chloride. Solvent was removed from the clear filtrate to yield 3.9 g (90%) of the crude *rac-*/*meso*-**3e** mixture. The diastereoisomers were separated as follows. The solid mixture was stirred with 40 mL of pentane. The *meso*-**3e** diastereomer dissolves predominantly under these conditions. The residue thus contained *rac*-**3e** and *meso*-**3e** in a 67:33 ratio; the diastereomeric ratio in the pentane filtrate was ca. 25:75. The residue was extracted two times with pentane (10 mL each) to give 250 mg of >97% pure *rac*-**3e**, mp 206 °C. From the first pentane extract a 250-mg sample was recovered which was recrystallized to give 170 mg of a ≥95% pure *meso*-**3e** sample. Anal. Calcd for $C_{32}H_{46}Cl_2Zr$ (*rac*-**3e**) (592.8): C, 64.83; H, 7.82. Found: C, 63.73; H, 7.80. IR (KBr): ν 3139, 3100, 2927, 1628 (C=C), 1446, 1097, 881, 842, 804 cm^{-1}. *rac*-**3e**: ^{1}H NMR (CDCl$_3$) δ 6.46, 6.11, 5.65 (m, 2H each, cyclopent CH), 5.27, 5.06 (AX, 2H each, C=CH_2), 3.15 (m, 2H, isopropyl CH), 2.25 (m, 2H, cyclohexyl CH), 1.88–1.68, 1.36–1.12 (m, 20H, cyclohexyl CH_2), 1.27, 1.16 (d, each 6H, isopropyl CH_3); ^{13}C NMR (CDCl$_3$, DEPT) δ 147.6 (C=CH$_2$), 141.1, 127.3 (ipso-C Cp), 117.8, 112.7, 108.6 (cyclopent CH), 109.7 (C=CH$_2$), 42.2 (cyclohexyl CH), 33.5, 33.1, 26.9, 26.8, 26.3 (cyclohexyl CH$_2$), 28.6 (isopropyl CH), 24.3, 21.9 (isopropyl CH$_3$), *meso*-**3e**: ^{1}H NMR (CDCl$_3$) δ 6.35, 6.12, 5.89 (m, 2H each, cyclopent CH), 5.30, 5.07 (AX, 2H each, C=CH_2), 3.03 (m, 2H, isopropyl CH), 2.23 (m, 2H, cyclohexyl CH), 1.94–1.71, 1.39–1.08 (m, 20H, cyclohexyl CH_2), 1.19, 1.15 (d, each 6H, isopropyl CH_3); ^{13}C NMR (CDCl$_3$, DEPT) δ 147.1 (C=CH$_2$), 142.1, 130.2 (ipso-C Cp), 113.9, 111.6, 109.8 (cyclopent CH), 109.6 (C=CH$_2$), 42.0 (cyclohexyl CH), 33.5, 33.2, 26.9, 26.4 (double intensity) (cyclohexyl CH$_2$), 28.9 (isopropyl CH), 23.4, 22.9 (isopropyl CH$_3$).

Preparation of the [(2,4,6-Triisopropylphenyl)sulfonyl]hydrazone of Cyclohexyl Methyl Ketone. [(2,4,6-Triisopropylphenyl)sulfonyl]hydrazine[13] (29.6 g, 100 mmol) and 11.4 g (90 mmol, 12.4 mL) of cyclohexyl methyl ketone were dissolved in a mixture of 70 mL of acetonitrile and 13 mL of concentrated HCl. The mixture was vigorously stirred overnight. The resulting reaction mixture was then chilled (−30 °C) and the resulting precipitate recovered by filtration. Recrystallization from acetonitrile/HCl (9:1) gave 22.8 g (56%) of the white crystalline product, mp 178–179 °C. Anal. Calcd for $C_{23}H_{38}N_2O_2S$ (406.6): C, 67.94; H, 9.42; N, 6.89. Found: C, 67.86; H, 9.61; N, 6.57. ^{1}H NMR (CDCl$_3$): δ 7.22 (s, 2H, arom CH), 4.74 (sept, 2H, *o*-CHMe$_2$), 2.62 (sept, 1H, *p*-CHMe$_2$), 1.71 (m, 1H, cyclohexyl CH), 1.42 (d, ^{3}J = 6.7 Hz, 12H, *o*-CH(CH_3)$_2$), 1.34–0.92 (m, 10H, cyclohexyl CH_2), 1.06 (d, ^{3}J = 6.9 Hz, 6H, *p*-CH(CH_3)$_2$). ^{13}C NMR (CDCl$_3$, APT): δ 159.2 (ipso-C Ph), 153.2, 151.0 (arom C(2), C(4), C(6)), 133.0 (C=N–), 123.8 (arom C(3), C(5)), 46.7 (double intensity), 34.4 (isopropyl CH), 30.2 (cyclohexyl CH), 30.0, 26.2, 26.1 (cyclohexyl CH$_2$), 25.1, 23.6 (isopropyl CH$_3$), 13.7 (CH$_3$).

1-(1-Cyclohexylethenyl)-3-methylcyclopentenol (8). A sample of 11.3 g (28.1 mmol) of the [(2,4,6-triisopropylphenyl)sulfonyl]hydrazone of cyclohexyl methyl ketone was dissolved in 100 mL of tetrahydrofuran, and the solution was cooled to −50 °C. To this solution was added 50 mL (65 mmol) of a 1.3 M *sec*-butyllithium solution in cyclohexane. The mixture turned orange-red. It was warmed to 0 °C and kept at this temperature until the gas evolution had ceased. The resulting red-brown solution of (1-cyclohexylvinyl)lithium (7) was cooled to −55 °C. To this solution was added dropwise 2.5 g (26.2 mmol) of 3-methylcyclopentenone. The mixture was warmed to room temperature, 10 mL of water was added, and then the solvent was removed in vacuo. To the red residue were added water and ether. The phases were separated, and the aqueous phase was extracted several times with ether. The combined ethereal solutions were washed with brine, and the solvent was evaporated to give 4.8 g (89%) of 8 as a yellowish oil which was only characterized by ^{1}H NMR spectroscopy and used without further purification. ^{1}H NMR (CDCl$_3$): δ 5.33 (m, 1H, H(2)), 5.10, 4.83 (AX, 1H each, C=CH_2), 2.36 (s, 3H, CH$_3$), 2.55–1.05 (m, 15H, cyclohexyl and five-membered ring CH$_2$).

[1-(1-Cyclohexylethenyl)-3-methylcyclopentadienyl]lithium (10). The crude 1-(1-cyclohexylethenyl)-3-methylcyclopentenol (8, 4.7 g, 22 mmol) was dehydrogenated by means of a vacuum distillation. Using a bath temperature of 125–160 °C a yellow oil (1.74 g, 42%, bp 75–85 °C, 10^{-2} Torr) was obtained which consisted of the double bond isomers of the (1-cyclohexylethenyl)-3-methylcyclopentadiene system (9) [^{1}H NMR (CDCl$_3$): δ 6.31, 6.22, 6.05, 5.83, 5.40, 5.17, 5.10, 5.05, 5.00, 4.93, 4.80, 4.75 (m, cyclopent CH and C=CH$_2$), 3.09, 3.03, 2.97 (m, cyclopent CH_2), 2.65–1.05 (m, cyclohexyl hydrogens and methyl)]. A sample (1.65 g, 8.9 mmol) of **9** was dissolved in 12 mL of ether. To this was added dropwise 5.1 mL (10.0 mmol) of a 1.93 M ethereal methyllithium solution. Methane evolution was observed, and a yellow precipitate was formed. After 2 h at room temperature the precipitate was filtered off and the clear filtrate concentrated in vacuo to about half its original volume. At 0 °C a slightly yellowish microcrystalline precipitate of **10** formed which was collected by filtration (yield 0.97 g, 56%). ^{1}H NMR (benzene-d_6/tetrahydrofuran-d_8 4:1): δ 6.07, 6.02, 5.78 (m, 1H each, Cp), 5.15, 4.53 (AX, 1H each, C=CH_2), 2.63 (m, 1H, cyclohexyl CH), 2.31 (s, 3H, CH$_3$), 1.80–1.65, 1.45–1.20 (m, 10H, cyclohexyl CH_2). ^{13}C NMR (benzene-d_6/tetrahydrofuran-d_8 4:1, APT): δ 153.0 (C=CH$_2$), 120.2, 115.1 (ipso-C Cp), 104.7, 102.6, 101.2 (cyclopent CH), 95.8 (C=CH$_2$), 43.3 (cyclohexyl CH), 34.7, 27.9, 27.4 (cyclohexyl CH$_2$), 15.6 (CH$_3$).

Bis[η-1-(1-cyclohexylethenyl)-3-methylcyclopentadienyl]zirconium Dichloride (3f). A solution containing 0.87 g (4.49 mmol) of the lithium reagent **10** in 25 mL of tetrahydrofuran was added dropwise at 0 °C to a suspension of 0.52 g (2.25 mmol) of ZrCl$_4$ in 30 mL of toluene. The mixture was then kept at 60 °C for 2 days. During this time a white precipitate had formed. Solvent was removed in vacuo. The pale yellow residue was taken up in 50 mL of dichloromethane and filtered from the lithium chloride. Evaporation of the solvent from the clear filtrate gave 1.07 g (88%) of a 54:46 mixture of *rac*-**3f** and *meso*-**3f**, mp 153–161 °C dec. Separation of the diastereomers was not achieved. An absolute assignment of the diastereomers was not possible. ^{1}H NMR (benzene-d_6): major isomer δ 6.23, 6.13, 5.74 (m, 2H each, cyclopent CH), 5.27, 4.99 (AX, 2H each, C=CH_2), 2.30 (m, 2H, cyclohexyl CH), 2.12 (s, 6H, Cp–CH_3), 1.95–1.05 (m, 20H, cyclohexyl CH_2); minor isomer δ 6.37, 6.05, 5.64 (m, 2H each, cyclopent CH), 5.27, 4.99 (AX, 2H each, C=CH_2), 2.30 (m, 2H, cyclohexyl CH), 2.28 (s, 6H, Cp–CH_3), 1.95–1.05 (m, 20 H, cyclohexyl CH_2). ^{13}C NMR (benzene-d_6, APT), mixture of isomers: δ 147.8, 147.5 (C=CH$_2$), 130.0, 129.6, 129.4, 128.9 (ipso-C Cp), 119.2, 116.3, 115.5, 115.3, 112.4, 110.1 (cyclopent CH), 109.6 (double intensity, C=CH$_2$), 42.44, 42.37 (cyclohexyl CH), 33.8, 33.7, 33.5, 27.2 (double intensity), 26.7 (cyclohexyl CH$_2$), 16.0, 15.8 (Cp–CH$_3$).

Photochemical Cyclization of 3a. NMR Experiments. A small sample (ca. 20 mg) of complex **3a** was dissolved in 0.6 mL of benzene-d_6, and the solution was irradiated in a 5-mm NMR tube for 4.25 h at 300–350 nm. ^{1}H NMR integration revealed the formation of a mixture containing 70% **11a** and 30% of the starting material **3a**. Further 300–350-nm irradiation did not change this ratio. For a second experiment 25 mg of the metallocene complex **3a** was dissolved in 0.6 mL of benzene-d_6 and photolyzed for 1 h at 450 nm. Within the limits of the ^{1}H NMR analysis complete conversion to the product **11a** was achieved. This solution was then photolyzed at 300–350 nm. After 3 h the 70:30 ratio of **11a**:**3a** was reestablished.

Preparative Scale Experiments. Complex **3a** (150 mg, 0.29 mmol) was dissolved in 5 mL of toluene and photolyzed for 3 h with 450-nm light. Solvent was then removed in vacuo. The orange-yellow residue with stirred with 5 mL of pentane overnight. Filtration gave 80 mg (55%) of **11a** as a pale yellow solid. Anal. Calcd for $C_{26}H_{34}Cl_2Zr$ (508.7): C, 61.39; H, 6.74. Found: C, 60.96; H, 6.81. IR (KBr): ν 2926, 2852, 1449, 1261, 1098, 1027, 802 cm^{-1}. ^{1}H NMR (benzene-d_6): δ 6.71, 6.22, 5.97, 5.72 (m, 2H each, cyclopent CH), 2.56 (m, 2H, cyclohexyl CH), 2.20–0.80 (m, 28H, cyclobutene CH_2 and cyclohexyl CH_2). ^{13}C NMR (benzene-d_6, APT): δ 138.2 (ipso-C Cp), 127.1, 116.3, 114.2, 107.5 (cyclopent CH), 59.9 (quart, C cyclobutene bridge), 46.4 (cyclopent CH), 31.1 (cyclobutene bridge CH$_2$), 28.6, 28.5, 27.2 (double intensity), 26.8 (cyclohexyl CH$_2$).

Photolysis of 3b. The photolysis of complex **3b** was only carried out on the NMR scale. A sample of 15 mg (0.03 mmol) of **3b** was dissolved in 0.6 mL of benzene-d_6, and the solution was transferred to a 5-mm NMR tube. Photolysis was carried out at 300–350 nm for 90 min. The formation of only 10% of the [2 + 2] cycloaddition product **11b** was observed by ^{1}H NMR spectroscopy. Prolonged irradiation led to a maximum amount of ca. 15% of **11a** in the photostationary equilibrium. Complex **11a** was only characterized by ^{1}H NMR spectroscopy as a minor component of the mixture of organometallic compounds after photolysis at 300–350 nm. ^{1}H NMR (benzene-d_6): δ 6.62, 6.33, 6.17, 5.64 (m, each 2H, cyclopent CH), 2.66, 2.36 (m, each 2H, cyclobutene bridge CH_2), the signals of the phenyl groups are hidden under those of **3a**.

Photolysis of 3d. *rac*-3d. The photolysis of this diastereomer was only carried out on a NMR scale, and the product was not isolated. The photolysis experiments were performed analogously to that described above for complex **3b**. A solution containing ca. 25 mg of *rac*-**3d** in benzene-d_6 was transferred to a NMR tube and photolyzed for 25 h at 300–350 nm. The resulting solution contained only ca. 5% *rac*-**11d**. A similar photolysis experiment using 254-nm light (quartz NMR tube) led to analogous results. In contrast, photolysis at 450 nm resulted in establishing a photostationary equilibrium containing *rac*-**11d** and *rac*-**3d** in a 53:47 ratio. Subsequent irradiation of this mixture using the 300–350-nm light source reestablished the 5:95 mixture of *rac*-**11d** and *rac*-**3d**. From the isolated 53:47 mixture complex *rac*-**11d** was characterized spectroscopically: ^{1}H NMR (CDCl$_3$) δ 7.23 (m, 10H, Ph), 6.60, 6.39, 6.35, 6.21, 6.04, 5.81 (m, each 1H, cyclopent CH), 3.20–2.70 (m, isopropyl CH and cyclobutene bridge CH_2), 1.31, 1.25, 1.19, 1.00 (d, each 3H, isopropyl CH_3); ^{13}C NMR (CDCl$_3$, APT) δ 145.9, 142.3, 138.2 (ipso-C Ph and Cp), 128.3, 128.0, 127.1, 126.1, 123.1 (Ph), 115.3, 114.0, 113.6, 112.8, 109.5, 106.8 (cyclopent CH), 60.3 (quart, C cyclobutene bridge), 33.2 (cyclobutene bridge CH$_2$), 28.9, 25.0 (isopropyl CH), 24.0, 23.2, 22.4, 21.1 (isopropyl CH$_3$). For *meso*-**3d** the wavelength-dependent photostationary equilibria were established by NMR experiments analogous to those described above. Photolysis (300–350 nm) led to a mixture of *meso*-**3d**, *meso*-**11d**, and *meso*-**11d′** in a 56:47:7 ratio; irradiation at 450 nm shifted this to 13:79:8.

Photolysis on a Preparative Scale. A solution of 150 mg (0.26 mmol) of *meso*-**3d** in 20 mL of toluene was photolyzed for 4 h at 450 nm to give a 79:8:13 mixture of *meso*-**11d**, *meso*-**11d′**, and *meso*-**3d**. Solvent was removed in vacuo and the residue treated with pentane to give 100 mg (67%) of a microcrystalline solid which consisted of >95% *meso*-**11d**, mp 187 °C dec. The filtrate was enriched in *meso*-**11d′** and *meso*-**3d**. Some of the starting material (*meso*-**3d**) precipitated from the pentane solution upon cooling (15 mg recovered). Anal. Calcd for $C_{32}H_{34}Cl_2Zr$ (*meso*-**11d**) (580.7): C, 66.18; H, 5.90. Found: C, 66.17; H, 6.25. IR (KBr): ν 2960, 1492, 1445, 1033, 843, 702 cm^{-1}. *meso*-**11d**: ^{1}H NMR (benzene-d_6) δ 7.25–6.86 (m, 10H, Ph), 6.32, 5.77 (m, 6H, cyclopent CH), 3.25 (sept, 2H, isopropyl CH), 2.82, 2.45 (m, each 4H, cyclobutene bridge CH_2), 1.16, 0.92 (d, each 6H, isopropyl CH_3); ^{13}C NMR (benzene-d_6, APT): δ 148.0 (ipso-C Ph), 146.6, 138.9 (ipso-C Cp), 128.3, 127.3, 126.4 (Ph), 115.6, 112.8, 107.9 (cyclopent CH), 60.7 (quart, C cyclobutene bridge), 33.3 (cyclobutene bridge CH$_2$), 29.2 (isopropyl CH), 23.5, 22.3 (isopropyl CH$_3$). *meso*-**11d′**: ^{1}H NMR (benzene-d_6) δ 6.61, 6.11, 5.86 (m, each 2H, cyclopent CH), 3.51 (sept, 2H, isopropyl CH), 2.72, 2.42 (m, each 2H, cyclobutene bridge CH_2), 1.39, 1.22 (d, each 6H, isopropyl CH_3), signals of the Ph group hidden.

Photolysis of 3e. The wavelength-dependent photostationary equilibria of **3e**/**11e** were determined analogously to that described above.

Photolysis on a Preparative Scale. A sample of *rac*-**3e** (100 mg, 0.17 mmol) was dissolved in 15 mL of toluene and then photolyzed at 300–350 nm for 90 min to give a 75:25 mixture of *rac*-**11e** and *rac*-**3e**. Solvent was removed in vacuo and the residue stirred with 5 mL of pentane. The starting material was thus dissolved and pure *rac*-**11e** remained, yield 60 mg (60%), mp 180–182 °C dec. Anal. Calcd for $C_{32}H_{46}Cl_2Zr$ (592.8): C, 64.83; H, 7.82. Found: C, 64.17; H, 7.97. IR (KBr): ν 2963, 2927, 1449, 1262, 1099, 841, 802 cm^{-1}. ^{1}H NMR (benzene-d_6): δ 6.63, 6.15, 6.01, 5.89 (double intensity), 5.85 (m, 1H each, cyclopent CH), 3.40, 3.26 (m, 1H each, isopropyl CH), 2.10–1.60 (m, 6H, cyclobutene bridge CH_2 and cyclohexyl CH), 1.42, 1.21, 1.18, 1.08 (d, each 3H, isopropyl CH_3), 1.20–0.90 (cyclohexyl CH_2). ^{13}C NMR (benzene-d_6, APT): δ 149.0 (double intensity), 141.4, 138.7 (ipso-C Cp), 115.0, 112.9, 111.6, 108.7, 106.2, 104.7 (cyclopent CH), 60.0 (quart, C cyclobutene bridge), 46.6, 46.5 (cyclohexyl CH), 33.7, 33.5, (cyclobutene bridge CH$_2$), 29.2, 28.6 (isopropyl CH), 31.2, 28.6, 28.5, 28.4, 28.2, 27.3 (double intensity), 27.0, 26.8, 25.2 (cyclohexyl CH$_2$), 23.6, 22.6, 22.1, 21.4 (isopropyl CH$_3$).

A solution of 50 mg (0.085 mmol) of *meso*-**3e** in 10 mL of toluene was photolyzed for 2 h at 450 nm. Removal of the solvent in vacuo gave the [2 + 2] cycloaddition product *meso*-**3e** quantitatively. Anal. Calcd for $C_{32}H_{46}Cl_2Zr$ (592.8): C, 64.83; H, 7.82. Found: C, 64.17; H, 7.81. ^{1}H NMR (benzene-d_6): δ 6.12, 6.07, 5.87 (m, 2H each, cyclopent CH), 3.28 (sept, ^3J = 6.9 Hz, 2H, isopropyl CH), 2.07 (m, 2H, cyclohexyl CH), 1.95–1.86 (m, 4H, cyclobutene bridge CH_2), 1.67–1.56 (m, 12H, cyclohexyl CH_2), 1.18, 1.08 (d, each 6H, isopropyl CH_3), 1.15–0.75 (m, 8H, cyclohexyl CH_2). ^{13}C NMR (benzene-d_6, DEPT): δ 148.7, 138.4 (ipso-C Cp), 115.7, 112.0, 104.9 (m, each 2H, cyclopent CH), 60.0 (quart, C cyclobutene bridge), 46.7 (cyclohexyl CH), 31.1 (cyclobutene bridge CH$_2$), 28.9, 28.1, 27.2 (double intensity), 27.0 (cyclohexyl CH$_2$), 23.4, 22.8 (isopropyl CH$_3$).

Photolysis of 3f. The photolysis was carried out on a NMR scale using a near to equimolar mixture of the **3f** diastereomers. A mixture of *rac*- and *meso*-**3f** (40 mg, 0.075 mmol, 54:46) was dissolved in benzene-d_6 and photolyzed in a 5-mm NMR tube for 10 h at 450 nm. Both photoproducts are formed in ca. 90% conversion. The assignment of the **11f** diastereoisomers was possible due to their different overall molecular symmetries. ^{1}H NMR (benzene-d_6, *rac*-**11f**): δ 6.45, 6.01, 5.97, 5.77, 5.72, 5.66 (m, 1H each, cyclopent CH), 2.34, 2.19 (s, 3H each, CH$_3$), 1.95–1.05 (m, 26H, cyclohexyl CH and CH$_2$ and cyclobutene bridge CH$_2$). ^{1}H NMR (benzene-d_6, *meso*-**11f**): δ 6.01, 5.97, 5.60 (m, 2H each, cyclopent CH), 2.19 (s, 6H, CH$_3$), 1.95–1.05 (m, 26H, cyclohexyl and –CH$_2$–CH$_2$–). ^{13}C NMR (benzene-d_6, DEPT, mixture of isomers): δ 140.7, 138.3 (ipso-C Cp), 126.1, 117.3, 116.7, 116.2, and 114.5 (both double intensity), 113.9, 107.5 (double intensity) (cyclopent *C*H), 60.05, 59.95 (quart, C cyclobutene bridge), 46.5, 46.3 (double intensity) (cyclohexyl *C*H), 31.2, 31.1, 31.0 (cyclobutene bridge *C*H_2), 28.8 (double intensity), 28.6, 28.4, 27.3, 26.8 (both double intensity) (cyclohexyl *C*H_2), 16.7 (double intensity), 14.7 (*C*H_3).

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Supplementary Material Available: Details of the X-ray crystal structure analyses of complexes **3c** and *rac*-**3d**, including listings of atomic fractional coordinates, thermal parameters, and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

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