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A Steroid-Substituted Group-4 Bent Metallocene System: Synthesis, Structural Features and Its Use in Catalytic Propene Polymerization☆

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3-Methoxyestra-1,3,5(10)-trien-16-one (**6**) was converted to the corresponding fulvene (**7**). Methyllithium was added and the resulting (16α-methylestratrienyl)cyclopentadiene **8** separated by chromatography. Deprotonation gave the (16α-methylestratrienyl-C_5H_4)Li reagent **9** that was added to 0.5 molar equivalents of $ZrCl_4(THF)_2$ to yield bis[η^5-(3-methoxy-16α-methylestra-1,3,5(10)-trien-16β-yl)cyclopentadienyl]zirconium dichloride (**10**, 45%). Complex **10** was activated by treatment with an excess of methylalumoxane. The resulting homogeneous Ziegler-type catalyst was employed for stereoselective propene polymerization. In the temperature range of −50 to −10°C partly isotactic polypropylene was obtained. A detailed analysis has revealed that stereocontrol is effected by a combination of enantiomorphic site and chain-end control. Compounds **7** and **10** were characterized by X-ray diffraction.

In a series of papers we have recently described the synthesis and structural properties of a variety of group-4 metallocene complexes bearing steroid- and terpene-derived substituents at the cyclopentadienyl, indenyl, or tetrahydroindenyl ring systems. It was shown that these substituents, which were employed optically active from chiral pool sources, may very effectively control the conformational equilibrium of the bis(indenyl)- and bis(tetrahydroindenyl)zirconium backbone. In several cases this characteristic was utilized to generate efficient homogeneous Ziegler-type catalysts from such complexes (by activation with an excess of methylalumoxane) for the selective formation of highly isotactic polypropylene[1]. The influence of the secondary and tertiary terpenyl and steroidal substituents at simple cyclopentadienyl ligands appears to be much less effective. We have recently shown that cholestan-3-yl-derived substituents [which very effectively controlled isotactic polypropylene formation at the substituted bis(indenyl)- and bis(tetrahydroindenyl)$ZrCl_2$-derived catalyst systems] were quite ineffective in doing so in the corresponding $(R^*\text{-}C_5H_4)_2ZrCl_2$/MAO catalyst systems (MAO = methylalumoxane). In the specific cases tested, no transfer of the metallocene chirality was obtained. The small degree of isotacticity observed was almost entirely due to stereochemical chain-end control taking place during the course of the catalytic polymerization reaction[2]. We have checked a few additional steroid substitution patterns of single chiral substituents attached to the cyclopentadienyl rings in such systems and found that the degree of chirality transfer may vary with the specific steroid substituent used. In addition the present study has also shown that an aromatic ethereal functional group attached to the far end of the steroid framework does neither adversely interfere with the generation of the homogeneous Ziegler catalyst system nor with the rapidly proceeding repetitive carbon-carbon coupling process taking place at the activated early transition metal center. A typical example is described in this paper.

Results and Discussion

Synthesis and Characterization of the Substituted Metallocene Complex

As a starting material for this study we have employed 3-methoxyestra-1,3,5(10)-trien-17-one (**1**). Unfortunately, we could not convert this sterically hindered ketone to the corresponding pentafulvene required for the straightforward synthesis of a steroid-substituted cyclopentadienyl ligand system[3]. Therefore, the keto functionality of **1** was shifted to the less hindered 16-position employing a slightly varied literature procedure[4]. The ketone **1** was subjected to a Shapiro reaction[5] via its tosylhydrazone **2**[6] to yield the steroidal tetraene system **3**. Bromohydrine formation followed by reductive debromination gave the alcohol **5** which was converted to the ketone **6** by Jones oxidation. The ketone was then treated with cyclopentadiene in the presence of pyrrolidine (fulvene synthesis according to the method of Stone and Little[7]) to produce the steroid fulvene **7**, which was isolated in 75% yield.

The fulvene **7** was obtained as yellow crystals after twice recrystallizing it from diethyl ether. It was characterized spectroscopically (^{13}C-NMR resonance signal of the positively polarized fulvene-carbon atom C-6 at δ = 159.7 in $CDCl_3$) and by X-ray diffraction. A view of the molecular geometry of the fulvene **7** is given in Figure 1. The bonding features of the steroid framework are unexceptional. The structural features of the fulvene moiety are as expected for a cross-conjugated triene system. Typical bond distances [Å] are as follows [for a comparison the corresponding carbon-carbon

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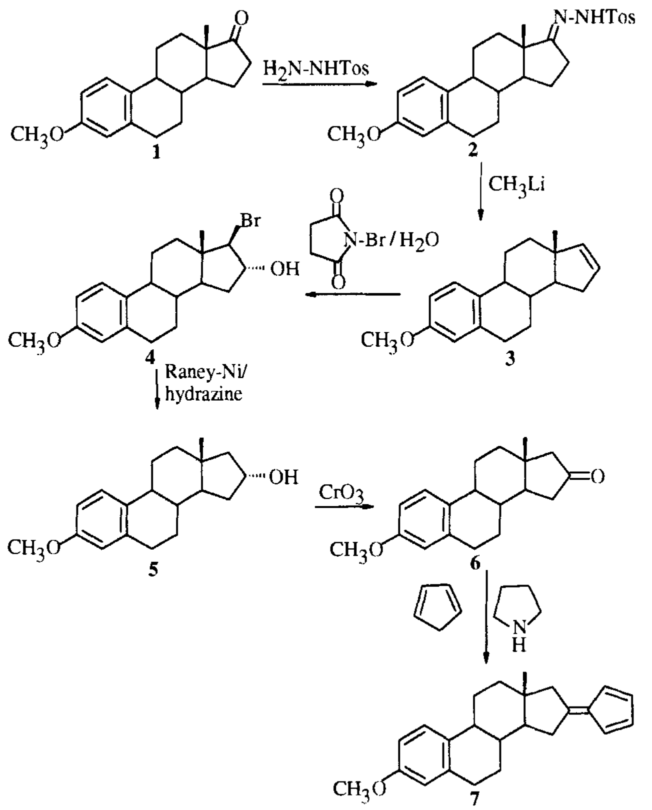


distances of the fulvene 5-(2,4-cyclopentadien-1-ylidene)cyclooctanone[8] are given in brackets]: 1.336(3) C(5)–C(6) [1.347(3)]; 1.455(4) C(1)–C(5), 1.454(4) C(4)–C(5) [1.464(3)]; 1.331(4) C(1)–C(2), 1.333(4) C(4)–C(3) [1.330(3)]; 1.454(5) C(2)-C(3) [1.451(3)]. The C–C–C bond angles within the fulvene five-membered ring of 7 are 109.1(3) [C(2)–C(1)–C(5)], 108.3(3) [C(1)–C(2)–C(3)], 109.0(3) [C(4)–C(3)–C(2)], 108.6(3) [C(3)–C(4)–C(5)]. The C(7)–C(6)–C(10) angle is 108.6(2)°.

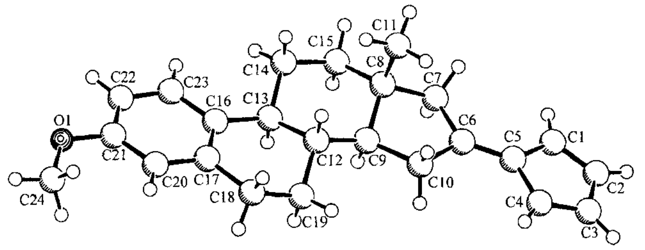
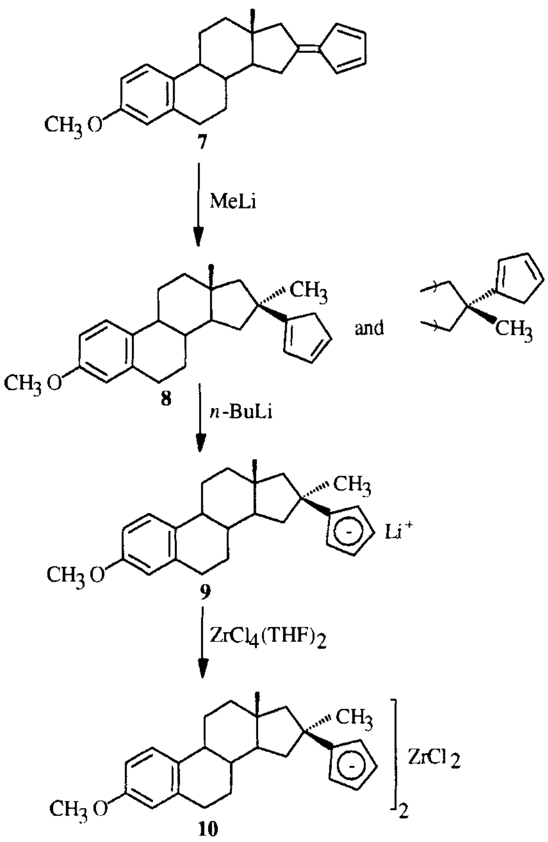


Figure 1. Molecular structure of the fulvene 7 (with unsystematical atom numbering scheme)

The fulvene 7 was treated with methyllithium. The substituted cyclopentadienyllithium compound was hydrolyzed by using wet ether to give the corresponding substituted cyclopentadiene systems. In this case two sets of diastereomers are formed which are distinguished by the relative configuration at the newly formed steroid stereogenic center (steroid carbon center C-16). The diastereomers are formed in a 3:1 ratio with the major isomer having the newly introduced methyl group attached in the α-orientation at the steroid center C-16. Each diastereomeric set is obtained as a mixture of cyclopentadienyl double bond isomers, of course (**8α** + **8α'**/**8β** + **8β'** = 3:1). The major diastereomeric components (**8α**, **8α'**) were separated from the minor congener by column chromatography. The **8α/8α'** mixture of double bond isomers was isolated in 36% yield.



The **8α/8α'** mixture of steroid-substituted cyclopentadienes was deprotonated by treatment with *n*-butyllithium in ether. The corresponding (R–C$_5$H$_4$)Li compound **9** was obtained as a white solid in >80% yield. It was used for the transmetalation reaction with zirconium without further characterization. The solid **9** was mixed with ZrCl$_4$(THF)$_2$ at −78°C, and then precooled toluene was added. The suspension was warmed to ambient temperature and then kept for several hours at 60°C to let the reaction go to completion. Workup gave the steroid-substituted zirconocene complex **10** in 45% yield. Complex **10** shows very characteristic NMR spectra. Attachment of the chiral substituent at the Cp-ring systems led to a diastereotopic differentiation of the remaining cyclopentadienyl methine units. In the ^{1}H-NMR spectrum ([D$_6$]benzene) these CH signals appear as multiplets centered at δ = 6.42, 6.34, and 6.26 in a 2:1:1 intensity ratio. In the ^{13}C-NMR spectrum there is a total of seven CH resonances corresponding to three arene and four cyclopentadienyl methine carbon atoms (δ = 126.2, 115.1, 114.5, 113.8, 113.5, 111.5, 111.4). There is only one set of estratrienyl-C$_5$H$_4$ ligand signals. We thus conclude that the Cp-subsituted zirconocene complex **10** behaves C_2-symmetrically in solution.

Complex **10** was characterized by an X-ray diffraction analysis (Figure 2). Crystals were obtained by slow room-temperature diffusion of pentane into a saturated solution of the zirconocene complex in dichloromethane. As expected, the zirconium center in **10** is pseudotetrahedrally coordinated to two monosubstituted η^5-cyclopentadienyl rings [Zr–D(1): 2.221, Zr–D(2): 2.205 Å; D(1) and D(2) denote the centroids of the cyclopentadienyl ring systems] and two chloride ligands [Zr–Cl(1): 2.455(3), Zr–Cl(2): 2.419(3) Å]. The D(1)–Zr–D(2) angle is 128.7°, the Cl(1)–Zr–Cl(2) angle 95.2(10)°. Both values are within the typical range of (RC$_5$H$_4$)$_2$ZrCl$_2$ complexes bearing monosubstituted cyclopen-

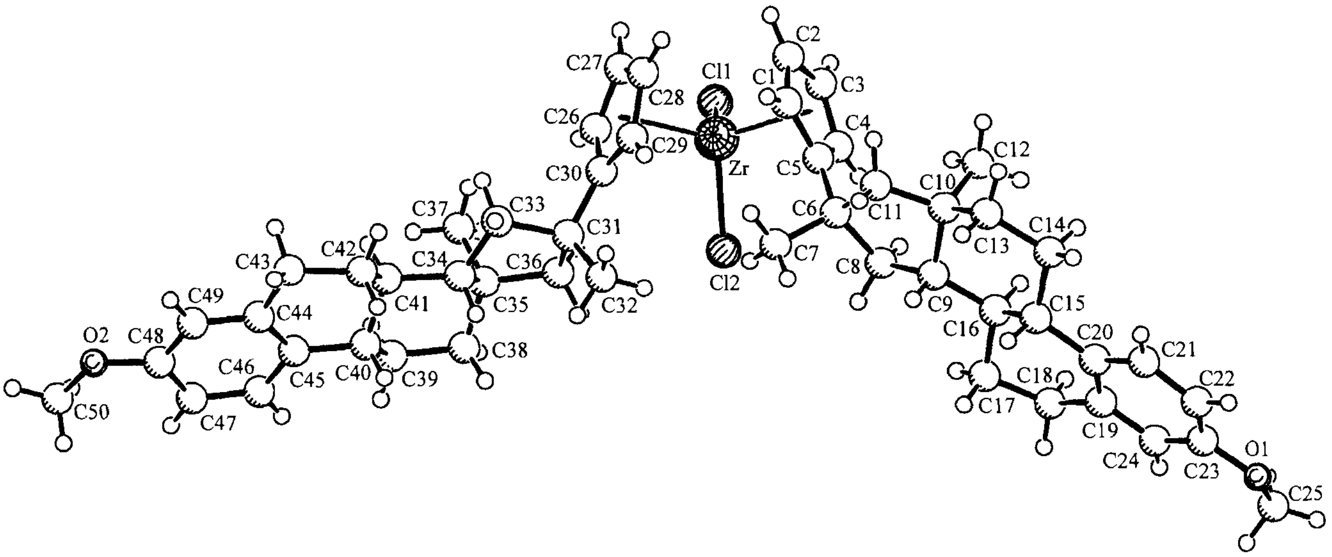


Figure 2. A view of the molecular structure of complex **10** in the crystal (with unsystematical atom numbering scheme)

tadienyl ligand systems[9]. The corresponding angles in bis(*tert*-butylcyclopentadienyl)$ZrCl_2$ are 128.6(8) [D−Zr−D*] and 94.2(6)° [Cl−Zr−Cl*], respectively[10].

In complex **10** the bulky substituents are attached to the Cp-ring carbon centers C(5) and C(30), respectively. The presence of these very large *tert*-cycloalkyl substituents has caused a marked distortion of the Zr-coordinated cyclopentadienyl ring systems. The Zr−C(5) linkage is rather long at 2.599(10) Å [Zr−C(30): 2.606(10)], whereas the adjacent cyclopentadienyl carbon atoms are much closer to the metal center at 2.490(10) [Zr−C(1)] and 2.537(8) Å [Zr−C(4)] [Zr−C(26): 2.535(8); Zr−C(29): 2.515(10) Å]. The Zr−C(2) and Zr−C(3) bonds are even shorter at 2.421(10) and 2.478(9) Å [Zr−C(27): 2.474(11), Zr−C(28): 2.477(12) Å].

The X-ray crystal structure analysis confirms that the newly introduced methyl substituent is attached to the α-face of the steroid framework. Major nucleophilic attack at the fulvene **7** has thus effectively been directed by the angular methyl substituent already present in the molecule at the junction of the C and D rings of **7** (see above). Thus, in the crystal structure analysis of **10** we observe that the pairs of methyl groups [C(7)/C(12) and C(32)/C(37), respectively; see Figure 2] are in a *trans* orientation. The cyclopentadienyl ring systems in **10** are β-attached to the steroid D rings.

Both estratrienyl groups rotate around the Cp-substituent σ-linkages [C(5)−C(6) and C(30)−C(31), respectively] such that the bulky steroidal frameworks are oriented away from the metal-containing core of the molecule. The steroid ring systems are oriented toward the outside of the bent metallocene framework. Both estratriene frameworks rotate such that their mean planes are arranged almost orthogonally to their attached cyclopentadienyl ring systems. Both bulky *tert*-cycloalkyl substituents are located in the lateral sectors of the bent metallocene unit, but it is quite remarkable that they are both oriented toward the same side of the bent metallocene wedge. This is a rather unusual conformational arrangement of a (*tert*-alkyl−C_5H_4)$_2ZrCl_2$ molecule. Normally, space-demanding R_3C substituents at the Cp ring systems favor a bis(lateral) conformational type which allows for a maximal spatial separation of the bulky groups attached to the η^5-cyclopentadienyl ligands at the group-4 metal atom[11]. In complex **10** the uncommon rotational arrangement is observed where the attached $R^1R^2R^3C$-type substituents exhibit a close to synperiplanar bis(lateral) conformation with a dihedral angle close to 30° {θ [C(5)−D(1)−D(2)−C(30): 30.8°]; θ [C(6)−D(1)−D(2)−C(31): 31.6°]}.

Propene Polymerization Reactions

Complex **10** was used to generate a homogenous Ziegler catalyst system for the stereoselective polymerization of propene. For this purpose the bent metallocene dihalide complex was dissolved in toluene and activated by treatment with a large excess of oligomeric methylalumoxane (MAO)[12]. For the experiments carried out during this study Al to Zr ratios ≥ 1000 were used. Polymerization reactions were carried out at three different temperatures.

At −50°C the polymerization activity of the **10**/MAO catalyst was very low (a = 70 [g polypropylene/g [Zr] · h). The resulting polypropylene (PP1) has a molecular mass of $\bar{M}_\eta$ = 115000. At −30°C the polymerization activity is much larger at a = 1160. As expected the average molecular mass of the isolated polypropylene sample (PP2) was decreased ($\bar{M}_\eta$ = 61000). At −10°C a further increased catalyst activity was observed (a = 1670), and the polymer molecular mass had further decreased ($\bar{M}_\eta$ = 35000).

The stereochemistry of the propene carbon-carbon coupling reaction at the **10**/methylalumoxane catalyst was monitored by ^{13}C-NMR spectroscopy and determined by statistical methyl pentade analysis analogously as described previously by us[1,13] and others[14]. The obtained polypropylenes (PP1-PP3) are all partially isotactic. The stereochemical control has to be attributed to a combined effect of the polymer chain end and the chiral metallocene backbone. The C−C coupling process at the **10**/MAO catalyst thus represents another example of stereochemical double stereodifferentiation in a polymerization process similar to a few examples that have recently been described by us[13]. It appears that the cooperative stereochemical control by the enantiomorphic site *and* the chain end is much more common than previously anticipated.

By means of a mathematical procedure recently described[13] we were able to formally separate the relative probabilities for the occurence of the effective stereocontrol exerted by the chiral metallocene backbone (ω) and the chain end (1-ω). At −50°C the calculated ω value is as high as 85%. It decreases slightly with increasing temperature (−30°C: 78%; −10°C: 63%). The isotacticity of the enantiomorphic site-controlled partition remains constant at α =

0.70 throughout this temperature range, whereas the effectiveness of chain end control to produce highly isotactic polypropylene decreases slightly with increasing temperature in this overall double stereodifferentiation-like situation (σ = 0.93 at −50°C, 0.83 at −30°C, 0.81 at −10°C).

This study has shown that there is a possibility of transforming a defined chirality information introduced at a bent metallocene complex by means of attaching specific steroid-derived substituents. Such substituents can readily be introduced from easily available estrone-type precursors. Of course, the resulting catalytic stereocontrol of such substituents is not sufficient for practical applications when they are attached to the simple Cp_2MX_2 systems. However, it is well conceivable that these very substituents will provide a valuable means of controlling the stereochemistry of catalytic CC-coupling processes when they are used either in open or ansa-bridged bis(indenyl) group-4 metal dihalide-derived homogeneous Ziegler catalyst systems.

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Experimental

Reactions employing organometallic compounds were carried out in an inert atmosphere (argon) by using Schlenk-type glassware or in a glove box. All solvents were dried and distilled under argon prior to use. Additional general information including a list of spectrometers is provided in refs.[1,13]. The propene polymerization reactions were carried out as was previously described in detail in refs.[1,13]. The ^{13}C-NMR pentade analysis of polypropylene was performed as previously described[1,13,14]. $ZrCl_4(THF)_2$ was prepared according to a literature procedure[15]. 3-Methoxyestra-1,3,5(10)-trien-17-onetosylhydrazone (**2**)[6], 3-methoxyestra-1,3,5-(10),16-tetraene (**3**), 17α-bromo-3-methoxyestra-1,3,5(10)-trien-16β-ol (**4**), and 3-methoxyestra-1,3,5(10)-trien-16β-ol (**5**)[4] were prepared as described in the literature.

3-Methoxyestra-1,3,5(10)-trien-16-one (**6**): To a solution of **5** (1.53 g, 5.34 mmol) in acetone (70 ml) was added at 10°C with stirring a solution of chromium(VI) oxide (0.33 g, 3.3 mmol) in 1.5 ml of 8 N H_2SO_4. After 10 min of stirring 3 ml of methanol was added. The reaction mixture was then poured into a saturated aqueous NaCl solution at 0°C. The precipitate was collected by filtration and washed with water until neutral. After recrystallization from ether (with charcoal) compound **6** was isolated in 84% yield (1.27 g). – ^{1}H NMR ($CDCl_3$): δ = 7.19 (d, ^3J = 8.8 Hz, 1H, 1-H), 6.72 (dd, ^3J = 8.8, ^4J = 2.7 Hz, 1H, 2-H), 6.63 (d, ^4J = 2.7 Hz, 1H, 4-H), 3.76 (s, 3H, OCH_3), 0.91 (s, 3H, 13-CH_3), 2.91–2.80 and 2.46–1.48 (m, 15H). – ^{13}C NMR ($CDCl_3$): δ = 55.1 (OCH_3), 18.1 (13-CH_3), 55.9, 39.0, 29.6, 28.1, 26.2, 26.0 (CH_2), 126.0, 113.8, 111.6 (arom. CH), 50.7, 43.7, 38.1 (steroid-CH), 218.1 (C=O), 157.7, 137.6, 132.1 (arom. C), 39.3 (steroid quart. C).

16-(2,4-Cyclopentadien-1-ylidene)-3-methoxyestra-1,3,5(10)-triene (**7**): To a suspension of **6** (1.27 g, 4.47 mmol) in 20 ml of anhydrous methanol and 3 ml of anhydrous ether was given at room temp. 1.5 ml (11.2 mmol) of freshly distilled cyclopentadiene. Pyrrolidine (0.56 ml, 6.72 mmol) was added dropwise. After 12 h of stirring the reaction mixture was hydrolyzed by adding 0.5 ml of glacial acetic acid and stirred for further 10 min. After addition of 20 ml of ether and 20 ml of water the organic layer was separated and the aqueous phase extracted five times with ether. The combined organic layers were washed with a saturated NaCl solution, dried, concentrated, and the crude product was crystallized from ether. The resulting fine yellow crystalline precipitate of the fulvene **7** was recovered by filtration and dried in vacuo to give 1.07 g (75%), m.p. 166°C. – IR (KBr): $\tilde{\nu}$ = 619 cm^{-1}, 630, 763, 790, 820, 860, 1038, 1047, 1233, 1245, 1312, 1365, 1462, 1501, 1603, 1653, 2845, 2870, 2903, 2918, 2932, 2951. – ^{1}H NMR ($CDCl_3$): δ = 7.20 (d, ^3J = 8.5 Hz, 1H, 1-H), 6.70 (dd, ^3J = 8.5, ^4J = 2.7 Hz, 1H, 2-H), 6.63 (d, ^4J = 2.7 Hz, 1H, 4-H), 6.48–6.35 (m, 4H, fulvene H), 3.77 (s, 3H, OCH_3), 0.82 (s, 3H, 13-CH_3), 3.14–1.38 (m, 13H). – ^{13}C NMR ($CDCl_3$): δ = 55.3 (OCH_3), 18.0 (13-CH_3), 38.6, 38.2, 33.2, 29.8, 28.0, 26.6 (CH_2), 130.3, 130.2, 126.2, 121.5, 121.2, 113.9, 111.5 (aromatic and fulvene-CH), 52.4, 43.8, 38.6 (steroid CH), 159.7 (C-16), 137.8 (fulvene C), 157.6, 132.5 (arom. C, 1 signal not observed), 40.9 (steroid quart. C). – $C_{24}H_{28}O$: calcd. 332.2140; found 332.2148 (MS).

X-Ray Crystal Structure Determination of **7**: A suitable crystal was obtained by slow crystallization of a saturated solution of the fulvene **7** in ether. The crystals formed as yellow thick needles. Molecular mass 332.46 g mol^{-1}, crystal size 0.20 × 0.25 × 0.50 mm, a = 11.608(2), b = 6.0940(4), c = 13.030(1) Å, β = 92.74(1)°, V = 920.7(2) Å^3, $d_{\text{calcd.}}$ = 1.199 g cm^{-3}, μ = 0.7 cm^{-1}, Mo-K_α radiation, λ = 0.171069 Å, $F(000)$ = 360 e, Z = 2, crystal system monoclinic, space group $P2_1$ (No. 4), Enraf-Nonius CAD4 diffractometer, scan mode $\omega-2\theta$, $[\sin\theta/\lambda]_{\max}$ = 0.62 Å^{-1}, 4152 measured reflections ($+h$, $\pm k$, $\pm l$), 2047 independent reflections, 1384 observed reflections $[I > 2\sigma(I)]$ for 228 refined parameters, structure solved by direct methods, H atoms calculated, R = 0.037, wR^2 = 0.085, residual electron density 0.14 eÅ^{-3}. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-58100, the names of the authors, and the journal citation.

1-[3-Methoxy-16α-methylestra-1,3,5(10)-trien-16β-yl]-cyclopentadiene (**8α,8α'**): A sample of 1.07 g (3.22 mmol) of the fulvene **7** was dissolved in 300 ml of ether, and the solution was cooled to −78°C. Then an ethereal solution of methyllithium (1.6 M, 3 ml, 4.8 mmol) was added dropwise. The reaction mixture was allowed to warm slowly to room temp. From the yellow solution a white product precipitated. After 12 h of stirring the cyclopentadienyllithium compound was collected by filtration, washed with ether and pentane. It was then hydrolyzed with wet ether and water, and the mixture was extracted several times with ether. The combined ethereal extracts were dried and concentrated to afford a yellow viscous oil of **8** (1.0 g), consisting of two diastereomers in a ratio of 3:1 (**8α** + **8α'**/**8β** + **8β'**), both of them as a mixture of two regioisomers. The two regioisomers of the major compound (**8α** + **8α'**) were separated by flash chromatography (silica gel, ethyl acetate/heptane, 1:4) (410 mg, 36%), whereas the minor compounds (**8β** + **8β'**) could not be isolated. – ^{1}H NMR ($CDCl_3$): δ = 7.19 (d, ^3J = 8.5 Hz, 1H, 1-H), 6.68 (dd, ^3J = 8.5, ^4J = 2.8 Hz, 1H, 2-H), 6.61 (d, ^4J = 2.8 Hz, 1H, 4-H), 6.55–5.91 (m, 3H, Cp-H), 3.76 (s, 3H, OCH_3), 2.96–2.92 (m, 2H, Cp-H), 1.25–1.23 (s, 3-H, 20-CH_3), 0.74/0.71 (s, 3H, 13-CH_3), 2.92–1.28 (m, 15H). – ^{13}C NMR ([D$_6$]benzene): δ = 134.2, 134.1, 132.4, 130.4, 124.0, 121.9 (Cp, both isomers), 126.6, 114.3, 111.9 (C-1,2,4), 54.8 (OCH_3), 55.7, 52.4, 44.3, 39.0, 37.8, 34.4, 33.2, 19.0 (steroid C), 137.9, 133.0 (arom. C), 55.7, 54.6, 42.9, 41.7, 41.3, 40.9, 40.5, 30.3, 30.2, 28.6, 27.0 (CH_2 and steroid C); two quaternary carbon atoms could not be detected.

Dichlorobis{η^5-[3-methoxy-16α-methylestra-1,3,5(10)-trien-16β-yl]cyclopentadienyl}zirconium (**10**): A solution of 600 mg (1.72 mmol) of the **8α**/**8α'** mixture in 50 ml of ether was cooled to 0°C. 1.34 ml of a solutoin of butyllithium in hexane (1.6 M, 2.14 mmol) was added dropwise. After warming to room temp. and stirring for 12 h, a white precipitate had formed which was collected by filtration. The precipitate was washed twice with small amounts of pentane and ether to give 524 mg of the cyclopentadienyllithium compound **9** (86% yield). This solid (450 mg, 1.27 mmol) was mixed with 239 mg (0.63 mmol) of $ZrCl_4(THF)_2$, and the mixture was cooled to −78°C. 50 ml of toluene, cooled to −78°C, was added to the mixture of the two solids. After stirring for 1 h at −78°C the suspension was allowed to warm to room temp. and stirred for another 12 h. For completion of the reaction the suspension was kept at 60°C for 3 h. After cooling to room temp. the suspension was filtered and the solution concentrated in vacuo. The residue was washed with 10 ml of pentane to give 245 mg (45% yield) of the white organometallic product **10**, m.p. 309°C (dec.). − IR (KBr): $\tilde{\nu} = 814\ \mathrm{cm^{-1}}$, 828, 1033, 1044, 1078, 1090, 1102, 1150, 1236, 1257, 1282, 1465, 1499, 1610, 2929, 2950, 2959, 3142. − ^1H NMR ($CDCl_3$): $\delta = 7.19$ (d, $^3J = 8.6$ Hz, 2H, 1-H), 6.69 (dd, $^3J = 8.6$, $^4J = 2.7$ Hz, 2H, 2-H), 6.61 (d, $^4J = 2.7$ Hz, 2H, 4-H), 6.47−6.38 (m, 4H, Cp-H), 6.38−6.30 (m, 2H, Cp-H), 6.30−6.22 (m, 2H, Cp-H), 3.76 (s, 6H, OCH_3), 1.49 (s, 6H, 16-CH_3), 0.84 (s, 6H, 13-CH_3), 2.88−2.74 and 2.45−1.43 (m, 30H). − ^{13}C NMR ($CDCl_3$): $\delta = 55.2$ (OCH_3), 31.8 and 19.7 (CH_3), 56.8, 43.9, 39.5, 29.8, 28.2, 26.7 (CH_2), 52.2, 43.9, 38.2, 126.2, 115.1, 114.5, 113.8, 113.5, 111.5, 111.4 (CH), 157.5, 146.8, 137.9, 132.9, 42.4, 41.8 (C). − $C_{48}H_{62}Cl_2OZr$ (857.2): calcd. C 70.06, H 7.29; found C 71.06, H 6.96.

X-Ray Crystal Structure Determination of **10**: A suitable crystal was obtained by slow room-temperature diffusion of pentane into a saturated solution of **10** in dichloromethane. The crystals formed as colorless thick needles. Molecular mass 857.12 g mol^{-1}, crystal size 0.35 × 0.22 × 0.15 mm, $a = 7.1990(4)$, $b = 21.909(2)$, $c = 27.356(4)$ Å, $V = 4314.7(8)$ Å^3, $d_{\mathrm{calcd.}} = 1.319\ \mathrm{g\ cm^{-3}}$, $\mu = 4.2\ \mathrm{cm^{-1}}$, Mo-$K_\alpha$ radiation, $\lambda = 0.71069$ Å, $F(000) = 1808$ e, $Z = 4$, crystal system orthorhombic, space group $P2_12_12_1$ (No. 19), Enraf-Nonius CAD4 diffractometer, scan mode $\omega-2\theta$, $[\sin\theta/\lambda]_{\max} = 0.59$ Å^{-1}, 4191 measured reflections ($+h$, $+k$, $+l$), 4141 independent reflections, 1853 observed reflections [$I > 2\sigma(I)$] for 502 refined parameters, structure solved by direct methods, H atoms calculated, $R = 0.047$, $wR^2 = 0.076$, residual electron density 0.36 eÅ^{-3}. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-58100, the names of the authors, and the journal citation.

☆ Dedicated to Professor *Helmut Werner* on the occasion of his 60th birthday.

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