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Group 4 metallocene complexes bearing cholestanol-derived substituents at the Cp-rings—their synthesis and use in propene polymerization catalysis

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Abstract

Two series of Group 4 bent metallocene complexes bearing cholestanol-derived substituents at their Cp-rings have been prepared. 5α-Cholestan-3α-ol was converted to the 3α-mesylate. Nucleophilic substitution with CpNa, followed by deprotonation and treatment with $ZrCl_4(THF)_2$ gave bis[η^5-(5α-cholestan-3β-yl)cyclopentadienyl]zirconium dichloride 3β-**5**. 5α-Cholestan-3-one **6** was converted to the corresponding fulvene, methyl lithium was added and deprotonation and addition to $ZrCl_4(THF)_2$ furnished bis[η^5-(3β-methyl-5α-cholestan-3α-yl)cyclopentadienyl]zirconium dichloride (**11b**). Treatment of the chiral Cp-substituted zirconocene dichlorides with a large excess of methyl alumoxane gave homogeneous Ziegler catalysts. Propene polymerization proceeded with overall stereochemical chain end control to give partly isotactic polypropylene.

Keywords: Zirconium; Cholestanol; Polymerization

1. Introduction

Homogeneous Group 4 bent metallocene/alumoxane Ziegler-type catalysts are increasingly being used for stereoselective α-olefin polymerization [1]. Commonly stereoselectivity is introduced to the system by employing rigid C_2-symmetric chiral ansa-metallocene backbones [2]. We have recently shown that chiral non-bridged zirconocene complexes can be used as well to achieve isotactic polypropylene formation under enantiomorphic site control [3]. Thus, catalysts derived from bis(indenyl)- or bis(tetrahydroindenyl)$ZrCl_2$ complexes which bear chiral substituents at the 1-positions of the η^5-bonded π-ligands also produce isotactic type-1 polypropylene (i.e. a polymer that contains only singular stereochemical "mistakes" statistically distributed along the chain). Terpenyl groups [4] and steroidal substituents [5] have been effectively used in this way. These substituents probably control the conformational properties of the rotationally flexible bent metallocenes [4,6]. There is evidence that in some cases metallocene rotamers are stabilized by those types of substituents that have their annulated six-membered rings of the central ligand system placed C_2-symmetrically in front of the bent metallocene wedge. In understanding the role of e.g. the chiral cholestanyl substituents it remained to be shown what their intrinsic influence on the stereochemistry of the polymer formation was, apart from controlling the bis(indenyl)zirconium conformer distribution. We have, therefore, prepared a few examples of simple bis(cholestanyl-Cp)-$ZrCl_2$ type complexes and looked at their performance in stereoselective propene polymerization.

2. Results and discussion

2.1. Synthesis of Cp-substituted metallocene complexes

We decided to investigate two series of cyclopentadienyl ligands with cholestanyl-derived substituents, one with a secondary and the other with a tertiary C3 cholestanyl carbon centre attached to the cyclopentadienyl ring system, and different synthetic routes were used for each. The starting material for both routes

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was 5α-cholestan-3β-ol (3β-**1**). This was converted to the mesylate 3β-**2** which was then treated with sodium cyclopentadienide in tetrahydrofuran to give a 25% yield of (5α-cholestan-3α-yl)cyclopentadiene (3α-**3**, 1:1.4 mixture of two isomers) [7]. Treatment with n-butyllithium in hexane afforded 3α-**4**. Its reaction with 0.5 molar equivalents of $ZrCl_4(THF)_2$ in tetrahydrofuran produced some of the derived zirconocene complex 3α-**5**. However, this metallocene could never be obtained pure; it was only characterized by ^1H NMR spectroscopy of a sample taken directly from the reaction mixture.

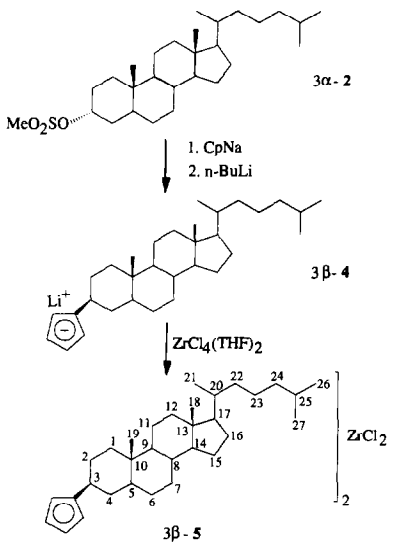
5α-Cholestan-3β-ol (3β-**1**) was oxidized to give 5α-cholestan-3-one (**6**) which was then converted to the 5α-cholestan-3α-ol epimer (3α-**1**) by treatment with lithium tris(sec-butyl)borohydride in tetrahydrofuran [8]. Conversion to the mesylate 3α-**2** followed by treatment with sodium cyclopentadienide gave (5α-cholestan-3β1-yl)cyclopentadiene in 62% yield as a 1:1.5 mixture of two regioisomers (3β-**3**). Deprotonation gave 3β-**4** which was then treated with $ZrCl_4(THF)_2$ to give bis[η^5-(5α-cholestan-3β-yl)cyclopentadienyl]zirconium dichloride (3β-**5**) in 38% yield. As expected, the zirconium complex 3β-**5** behaves in a C_2-symmetric manner in solution. In the ^{13}C NMR spectrum in [d_6]benzene at ambient temperature it exhibits three signals of the Cp-methine carbon atoms at δ 114.5 (double intensity), 112.0, and 112.2 (one of the $C^{\alpha}/C^{\alpha'}$ and $C^{\beta}/C^{\beta'}$ diastereotopic pairs is not separated) and the respective quarternary Cp-carbon resonance at 140.7. Only one set of cholestanyl signals is observed in the ^{13}C NMR spectrum, as well.

The other ligand type used in this study was prepared starting from 5α-cholestan-3-one (**6**). It was converted to the fulvene **7** by means of the procedure introduced by Stone and Little, i.e. by reacting **6** with cyclopentadiene with the aid of pyrrolidine [9]. The fulvene was isolated (72% yield) and then treated with methyl lithium. The methyl nucleophile added cleanly to the positively polarized fulvene carbon atom which is identical with the cholestanyl C3 centre [10]. After quenching with water the product was obtained as a 1:1 mixture of double bond shifted regioisomers (**8**). Deprotonation of **8** (n-butyl lithium in hexane) produced a single isomer of the cyclopentadienide system that contains the *tert*-cholestanyl substituent attached to it. In the ^{13}C NMR spectrum of the lithium compound **9** the signal of the newly introduced methyl group at C3 is observed at δ 38.5 (in [d_6]benzene/[d_8]tetrahydrofuran, 8:2). The Cp-methine carbon atoms give rise to two signals at δ 101.9 and 101.5 of equal intensity. The corresponding quarternary Cp-carbon centre shows a signal at δ 121.0. Apparently the chirality already present in the fulvene **8** has very effectively directed the stereoselective formation of a new stereogenic centre at C3. We assume that the methyl nucleophile approach to the sp^2-carbon atom C3 in **8** is similarly controlled as it has been observed in related additions to a keto group at C3 in the steroid system, preferring nucleophilic attack from the β-side [11]. We thus conclude that addition of methyl lithium to the fulvene **8** has taken place diastereoselectively to give only (3β-methyl-5α-cholestan-3α-yl)cyclopentadienyl lithium (3α-**9**).

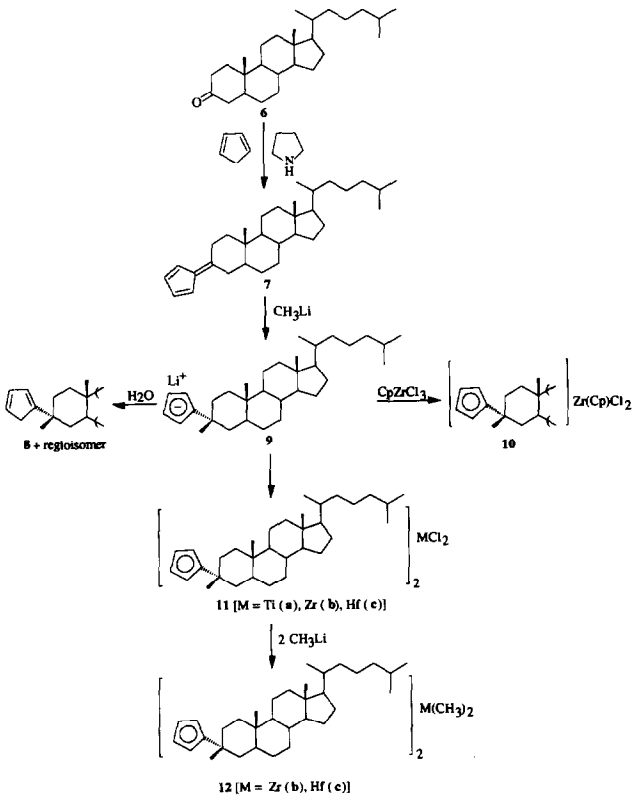
In contrast to 3α-**4**, the 3α-**9** reagent could easily and in satisfactory yield be attached to Group 4 transition metals. First, we treated 3α-**9** with (η-cyclopentadienyl)zirconiumtrichloride [12]. Reaction of the bulky RCp^- nucleophile needed some time at 60°C before its eventual completion. Finally, the $Cp(CpR)ZrCl_2$ product **10** was isolated in > 70% yield. The ^{13}C NMR spectrum of **10** (in [d_6]benzene) shows a Cp-singlet at δ 115.8 and the signals of the substituted RCp-ring system at δ 118.5 (CH, diastereomeric $C^{\beta}/C^{\beta'}$ not separated), 112.5, 110.4 (CH, $C^{\alpha}/C^{\alpha'}$), and 141.4 (*ipso*-C).

The RCp-Li reagent 3α-**9** was then treated with $ZrCl_4(THF)_2$ [13]. The two components were mixed at −78°C, then stirred for a while at room temperature and finally kept for ca. 6 h at 60°C to ensure completion of the reaction. Workup then gave 71% of the $(RCp)_2ZrCl_2$ product **11b**. In solution the metallocene complex **11b** again appears as C_2-symmetric. In the ^{13}C NMR spectrum ($CDCl_3$) only a single set of RCp resonances is observed, featuring six methyl singlets (at δ 33.2, 22.9, 22.5, 18.7, 12.1, and 12.0) and four signals of the diastereotopic cyclopentadienyl *C*H's at δ 119.4, 119.2, 111.8, and 109.6 (quart. C at 140.9).

The corresponding hafnium compound **11c** was prepared analogously by reacting the (3β-methyl-5α-cholestan-3α-yl)cyclopentadienyllithium reagent **9** with hafnium tetrachloride. The bent metallocene complex



Scheme 1.



Scheme 2.

11c was isolated as a white solid in 45% yield. The titanium complex **11a** was similarly prepared using toluene instead of tetrahydrofuran as a solvent. This product was isolated in ca. 60% yield.

To further characterize the symmetry features of these complexes in solution, a small sample of the Cp-substituted zirconocene dichloride **11b** was converted to the corresponding zirconocene dimethyl complex **12b** by treatment with excess ethereal methyl lithium. Complex **12b** was characterized by temperature dependent ^1H and ^{13}C NMR spectroscopy. In the temperature range tested (ambient temperature to −30°C, at lower temperatures **12b** is rapidly precipitated from [d_8]toluene or [d_2]dichloromethane solutions) only a single set of Cp–(Me-cholestanyl) NMR resonances is observed in addition to a singlet of the $Zr(CH_3)_2$ moiety ($^1H/^{13}C$ NMR: δ 0.13/31.2). The dimethylmetallocene symmetry probe thus confirms the presence of a C_2-symmetric structure of these complexes in solution or the very rapid equilibration of metallocene rotamers of lower symmetry, respectively. The Cp-substituted hafnocene dimethyl complex **12c** was prepared analogously, and it shows the same NMR behaviour.

2.2. Propene-polymerization reactions

From the compounds described above the complexes dichlorobis[η^5-(5α-cholestan-3β-yl)cyclopentadienyl]zirconium (3β-**5**) and dichlorobis[η^5-(3β-methyl-5α-cholestan-3α-yl)cyclopentadienyl]zirconium (**11b**) were employed to generate active homogeneous Ziegler-type catalysts for propene polymerization [1,2].

The Cp-3β-cholestanyl substituted system 3β-**5** was dissolved in toluene and activated by adding an excess of the oligomeric methyl alumoxane (MAO) [Al:Zr ratio ≈ 2000]. The mixture was kept by thermostat at −10°C and then propene was added and polymerized during 3 h. The reaction mixture was then quenched with methanol and the polypropylene isolated. Under these conditions the gross polymerization activity of the 3β-**5**/MAO catalyst was $a = 3800$ g polymer/g [Zr] · h. The polymer (PP1) has a molecular weight of $\overline{M}_\eta \approx 100\,000$. Two additional polymerization experiments were carried out at lower temperature with the aid of an even larger excess of methyl alumoxane (for details see Table 1). At −30°C polypropylene with a molecular weight of close to $\overline{M}_\eta \approx 300\,000$ was formed with high catalyst activity. At −50°C the activity dropped as expected and the molecular weight of the polypropylene had increased to about $\overline{M}_\eta \approx 500\,000$.

The stereochemical composition of the polypropylene samples obtained was monitored by ^{13}C NMR spectroscopy and characterized by a methyl pentade analysis using published procedures [3,4,14]. The selected spectrum shown in Fig. 1 shows the ^{13}C NMR methyl resonances of the polypropylene sample PP3, obtained by carrying out the catalytic olefin coupling at −50°C at the 3β-**5**/MAO catalyst. The three prominent peaks belong to the mmmm (left), mmmr, and

Table 1
Details of propene polymerization reactions with catalyst systems derived from 3-cholestanyl-substituted zirconocenes

metallocene	temp (°C)	polymer	mg Zr-cat.	mmol cocat.	Al/Zr	cat. activity [a]	$\overline{M}_\eta$	σ
3β-**5**	−10	PP1	12	24.2	2086	3840	105 000	0.71
3β-**5**	−30	PP2	1.9	24.2	12740	18500	294 000	0.71
3β-**5**	−50	PP3	1.9	24.2	12740	2300	502 000	0.72
11b	−10	PP4	20	24.2	1290	248	48 000	0.72
11b	−30	PP5	20	24.2	1290	598	62 000	0.76
11b	−50	PP6	18	24.2	1430	707	237 000	0.80

[a] g polymer/g [Zr] · h; polymerization reactions were carried out for 3 h each, except PP5 (2.8 h).

mmrm methyl pentades, the latter two are found in a close to 1:1 ratio (rel. ratios: 0.21/0.20/0.22, remaining intensity goes to the smaller signals). Thus the obtained polypropylene has an isotactic block structure (type 2) [15], although it is to be regarded as of rather low isotacticity. The dominating stereocontrol is therefore by the chiral end of the growing polymer chain. The chirality of the bent metallocene itself, introduced by the attachment of the chiral steroid substituents, is close to negligible. The same is observed with the polymerization reactions at higher temperatures. In all cases stereochemical chain end control prevails with probabilities σ to find m dyads of around 70% [PP1 (−10°C): $\sigma = 0.71$; PP2 (−30°C): $\sigma = 0.71$; PP3 (−50°C): $\sigma = 0.72$].

Propene polymerization reactions with the **11b**/methylalumoxane catalyst were also carried out at three different temperatures. [Al]:[Zr] ratios of ca. 1300–1400 were employed. Overall the catalyst activities were much smaller employing the *tert*-alkyl substituted Cp-system with the cyclopentadienyl ring in the α-orientation (**11b**) as compared to the 3β-**5** derived system which has the Cp-ring β-attached at a secondary cholestanyl position. In the temperature range employed the activity of the **11b**/MAO catalyst increased with decreasing temperature [PP4 (−10°C): $\alpha \approx 250$; $\overline{M}_\eta \approx 48000$; PP5 (−30°C): $\alpha \approx 600$; $\overline{M}_\eta \approx 62000$; PP6 (−50°C): $\alpha \approx 700$; $\overline{M}_\eta \approx 230000$]. Again the stereochemistry of the polymerization process is governed almost entirely by chain end control [rel. intensities: PP4 (−10°C), mmmm 0.26, mmmr 0.21, mmrm + rmrr 0.24; PP5 (−30°C), mmmm 0.24, mmmr 0.23, mmrm + rmrr 0.21; PP6 (−50°C), mmmm 0.42, mmmr 0.20, mmrm + rmrr 0.23]. As can be seen from these values and a comparison of the respective ^{13}C NMR methyl pentade signals (see Fig. 2), there appears to be a tendency to slightly higher isotacticities of the "type 2" block polymer formation with decreasing temperature [PP4: $\sigma = 0.72$; PP5: $\sigma = 0.76$; PP6: $\sigma = 0.80$].

This study has shown that the secondary and tertiary 3-cholestanyl substituents attached to a simple cyclopentadienyl ring system do not effectively transfer their inherent chirality directly during the catalytic carbon–carbon coupling which leads to polypropylene. It appears as if these substituents behave just like many other ordinary achiral sec- or *tert*-alkyl substituents, respectively. Therefore, the role of these chiral substituents at the corresponding substituted bis(indenyl)-metallocene systems, where their presence leads to high enantiomorphic site control [5], as indicated in the introductory paragraph, seems to be predominantly due to their ability to control very effectively the conformational properties of the bis(indenyl)zirconocene derived catalyst systems [4]. It appears that the 3-cholestanyl substituents are very efficient in determining a favourable rotameric distribution; how they control the stereochemical outcome of carbon-carbon coupling processes at such catalyst systems is therefore rather subtle and indirect.

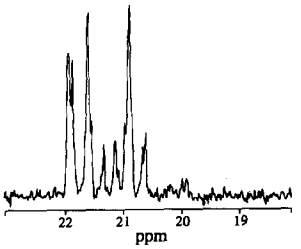


Fig. 1. ^{13}C NMR methyl pentade signals of polypropylene (PP3) obtained with the 3β-**5**/methylalumoxane catalyst at −50°C (NMR spectrum in 1,2,4-trichlorobenzene at 350 K).

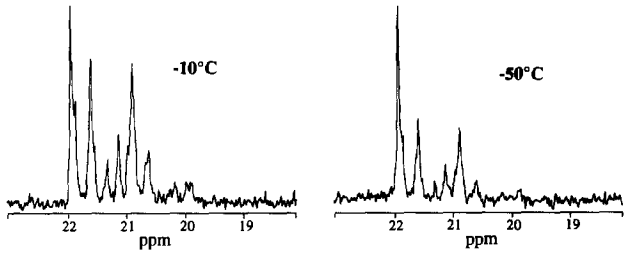


Fig. 2. A comparison of the ^{13}C NMR methyl pentade resonances of polypropylenes PP4 (prepared with the **11b**/methyl alumoxane catalyst at −10°C) and PP6 (−50°C). Spectra in 1,2,4-trichlorobenzene at 350 K.

3. Experimental details

3.1. General conditions

Reactions with organometallic compounds were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glove box. Solvents were dried and distilled under argon prior to use. For additional general information including a listing of spectrometers and equipment used for physical characterization see refs. [4]. 5α-Cholestan-3β-ol was employed as purchased. $CpZrCl_3$ [12] and $ZrCl_4(THF)_2$ [13] were prepared as described in the literature. The propene polymerization reactions were carried out as previously described in detail [4–6]. The ^{13}C NMR pentade analysis of polypropylene and the statistical analysis were performed as described previously. For leading references concerning the functional group transformations at the A-ring of the steroid backbone see ref. [11].

3.2. Preparation of cholestan-3-one (6)

A solution of chromium(VI)oxide (2.3 g, 23 mmol) in 8.6 ml of 8 N H_2SO_4 was added to a solution of α-cholestan-3β-ol 3β-**1** (12.0 g, 31 mmol) in acetone

(400 ml) at 10°C with stirring. After 5 min 15 ml of methanol was added. The reaction mixture was then poured into a saturated aqueous solution of NaCl at 0°C. The precipitate was collected by filtration and washed with water until neutral. After recrystallization from diisopropylether, compound **6** was isolated in 80% yield (9.5 g), m.p. 130°C. ^{1}H NMR ($CDCl_3$): δ = 2.5–0.6 (m). ^{13}C NMR ($CDCl_3$): δ = 212.1 (C3). IR (C=O): $\tilde{\nu}$ = 1714 cm^{-1}.

3.3. Preparation of 5α-cholestan-3α-ol (3α-1)

To a solution of 5α-cholestan-3-one **6** (3.6 g, 7.75 mmol) in 10 ml THF was added dropwise at 0°C a 1 M solution of lithiumtris(sec-butyl)borhydride in THF (12 ml, 12 mmol). The reaction mixture was stirred during 4 h at 0°C and then hydrolyzed with 4 ml of 3 M aqueous NaOH solution containing 4 ml H_2O_2 (30%). After stirring at room temperature for 30 min, the organic layer was separated and the aqueous phase extracted five times with ether. The combined organic phases were dried over $MgSO_4$ and concentrated to yield 2.3 g (82%) of the product (3α-**1**). ^{1}H NMR ($CDCl_3$): δ = 4.02 (m, $\omega_{1/2}$ = 11 Hz, 1H, 3-H), 2.0–0.6 (m, 46H, cholestanyl-H).

3.4. Preparation of 5α-cholestan-3α-yl-methansulfonate (3α-2)

To a solution of 5α-cholestan-3α-ol (3α-**1**) (14.0 g, 36.0 mmol) in 140 ml of dry pyridine at 0°C was added dropwise 28.0 g (360.0 mmol) of methansulfonylchloride. The reaction mixture was stirred at 0°C for 3 h and then poured into 500 ml of ice. After 1 h the precipitate was separated, dissolved in ether and washed first with 2 N H_2SO_4, then with saturated aqueous sodium bicarbonate solution and finally with water. After recrystallization from acetone the product (3α-**2**) was obtained in 60% yield (11.1 g), m.p. 113°C. ^{1}H NMR ($CDCl_3$): δ = 4.96 (m, $\omega_{1/2}$ = 7 Hz, 1H, 3-H), 2.98 (s, 3H, SO_2-CH_3), 1.98–0.58 (m, 46H, cholestanyl-H).

3.5. Preparation of 5α-cholestan-3β-yl-methansulfonate (3β-2)

5α-Cholestan-3β-yl-methansulfonate (3β-**2**) was prepared in a similar manner. Starting from 5α-cholestan-3β-ol (18.0 g, 46 mmol) the product 3β-**2** was obtained in 60% yield (13.0 g), m.p. 114°C. ^{1}H NMR ($CDCl_3$): δ = 4.59 (m, $\omega_{1/2}$ = 23 Hz, 1H, 3-H), 2.97 (s, 3H, SO_2-CH_3), 1.96–0.60 (m, 46H, cholestanyl-H).

3.6. Preparation of (5α-cholestan-3β-yl)cyclopentadiene (3β-3)

To a suspension of 0.7 g (30 mmol) finely dispersed sodium in THF was added dropwise at 0°C a solution of freshly distilled cyclopentadiene (2.5 ml, 30 mmol) in 40 ml of THF. After the sodium was dissolved, a solution containing 9.4 g (21 mmol) of 5α-cholestan-3α-yl-methansulfonate (3α-**2**) in 50 ml of THF was added at 0°C. The reaction mixture was stirred for 4 h at 0°C, warmed to room temperature and kept for another 24 h. For completion of the reaction, the mixture was heated to reflux for 2 h. After cooling to room temperature the reaction mixture was hydrolyzed with water and extracted with ether, dried and concentrated. Recrystallization from ether gave 62% yield (5.7 g) of 3β-**3** as a mixture of two regioisomers in a 1 to 1.5 ratio, m.p. 113°C. ^{1}H NMR ($CDCl_3$): δ = 5.96–5.95 (m), 6.13–6.11 (m), 6.43–6.37 (m), 6.52–6.49 (m), 2.93–2.87 [m, cyclopentadienyl, both isomers, 1-H, (Cp)], 2.43–2.22 (m, cholestanyl-3-H), 1.99–0.63 (m, cholestanyl-H). ^{13}C NMR ($CDCl_3$): δ = 155.5, 152.6 (quart. C, Cp), 42.6, 35.8, 35.9 (quart. C, cholestanyl) 133.7, 133.4, 132.3, 130.1, 124.0, 123.5 (CH, Cp), 56.6, 56.4, 54.7, 46.8, 46.8, 40.0, 39.0, 35.9, 35.6, 28.0 (CH, cholestanyl), 41.5, 41.0, 40.2, 39.6, 38.7, 38.6, 36.2, 35.9, 35.0, 32.2, 29.2, 29.0, 28.3, 28.1, 28.0, 24.2, 23.9, 21.1 (CH_2, Cp and cholestanyl), 22.8, 22.6, 18.7, 12.4, 12.1 (CH_3, cholestanyl). Anal. calcd. for $C_{32}H_{52}$ (M = 436.8) C 88.00, H 12.00; found C 86.86, H 12.41%.

3.7. Preparation of (5α-cholestan-3α-yl)cyclopentadiene (3α-3)

(5α-Cholestan-3α-yl)cyclopentadiene (3α-**3**) was obtained in a similar manner. Reaction of 0.78 g (33 mmol) of sodium and 2.8 ml (33 mmol) of cyclopentadiene with 11.7 g (25 mmol) of 5α-cholestan-3β-yl-methansulfonate (3β-**2**) in THF yielded 3.0 g (25% yield) of 3α-**3** as a viscous oil. The ratio of the two double bond isomers (A, B) was 1 to 1.4. ^{1}H NMR ($CDCl_3$): δ = 6.53–6.48 (m, 0.7H, Cp–H, A), 6.47–6.43 (m, 1H, Cp–H, B), 6.43–6.36 (m, 0.7H, Cp–H, A), 6.28–6.21 (2H, Cp–H, B), 6.10–6.05 (0.7H, Cp–H, A), 3.02–2.97 (m, 1.4H, $CpCH_2$, A), 2.88–2.85 (m, 2H, $CpCH_2$, B), 2.83–2.65 (m, 1.7H, 3-H), 2.0–0.5 (m, 78H, cholestanyl-H). ^{13}C NMR ($CDCl_3$): δ = 153.5, 150.4, 134.5, 133.2, 132.4, 130.2, 126.4, 125.8 (quart. C, Cp), 56.6, 56.4, 56.3, 54.5, 54.5, 42.7, 42.6, 41.4, 41.1, 40.9, 40.1, 39.5, 36.4, 36.3, 36.2, 35.8, 35.5, 34.9, 34.2, 33.6, 33.0, 32.1, 32.0, 29.0, 28.3, 28.0, 25.5, 24.9, 24.2, 23.9, 22.8, 22.6, 20.8, 18.7, 12.1, 11.9.

3.8. Preparation of 3-(2,4-cyclopentadien-1-ylidene)-5α-cholestane (7)

To a suspension of 5α-cholestan-3-one **6** (2.50g, 6.46 mmol) in 15 ml of abs. methanol and 3 ml of abs. ether was added 1.06 g (1.33 ml, 16.5 mmol) of freshly distilled cyclopentadiene at room temperature. Pyrrolidine (0.71 g, 0.83 ml, 10 mmol) was added dropwise.

After 12 h of stirring the reaction mixture was hydrolyzed by adding 2 ml of glacial acetic acid and stirred for another 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 saturated NaCl solution, dried, concentrated, and recrystallized from ether. The resulting fine yellow crystalline precipitate of the fulvene compound **7** was recovered by filtration and dried in vacuo to give 2.0 g (72%), m.p. 121°C dec. ^{1}H NMR ($CDCl_3$): δ = 6.60–6.52 (m, 2H, fulvene-H), 6.52–6.43 (m, 2H, fulvene-H), 0.95 (s, 3H, 19-H), 0.88 (d, 3H, ^3J = 7.3 Hz, 21-H), 0.84 (d, 6H, ^3J = 7.3 Hz, 26-H/27-H), 0.65 (s, 3H, 18-H), 3.01–0.60 (m, 27H, cholestanyl-H). ^{13}C NMR ($CDCl_3$): δ = 22.8, 22.7, 18.7, 12.1, 12.0 (cholestanyl-CH_3), 40.3, 40.0, 39.5, 36.3, 36.2, 32.0, 29.5, 29.1, 28.2, 24.2, 23.8, 21.2 (cholestanyl-CH_2), 130.5, 130.5, 119.9, 119.8 (fulvene-CH), 56.4, 56.2, 54.2, 48.4, 35.8, 35.4, 28.0 (cholestanyl-CH), 158.3 (quart. C, fulvene), 139.1, 42.6, 36.5 (cholestanyl-C). IR (KBr): $\tilde{\nu}$ = 617, 769, 1028, 1085, 1369, 1383, 1444, 1456, 1465, 1637, 2846, 2866, 2927, 2931, 2945, 2950 cm^{-1}. Anal. calcd. for $C_{32}H_{46}$(M = 434.8) C 88.41, H 11.59; found C 88.52, H 11.89%.

3.9. Preparation of (3β-methyl-5α-cholestan-3α-yl)-cyclopentadiene(8)

1.00 g (2.30 mmol) of 3-(2,4-cyclopentadien-1-ylidene)-5α-cholestane **7** was dissolved in 40 ml of ether and cooled to −78°C. An ethereal solution of methyl lithium (1.6 M, 1.6 ml, 2.75 mmol) was added dropwise. The reaction mixture was allowed to warm slowly to room temperature. From the yellow solution a white precipitate was formed. After 12 h of stirring, the cyclopentadienyllithium compound was collected by filtration, washed with ether and pentane. The lithium compound was hydrolyzed with water and extracted with ether. The combined ethereal extracts were dried, concentrated, and gave **8** as a yellow viscous oil (0.85 g, 82%). The ratio of the double bond regioisomers was 1 to 1. ^{1}H-NMR ($CDCl_3$): δ = 6.61–5.97 (m, 3H, Cp-H, A and B), 3.00–2.95/2.86–2.81 (m, 2H, Cp-H), 1.11/1.10 (s, 3H, 28-H), 0.79 (s, 3H, 19-H), 0.88 (d, 3H, ^3J = 5.6 Hz, 21-H), 0.85 (d, 6H, ^3J = 6.5 Hz, 26-H/27-H), 0.63 (s, 3H, 18-H), 3.01–0.60 (m, 27H, cholestanyl-H).

3.10. Preparation of (5α-cholestan-3β-yl)cyclopentadienyllithium (3β-4)

To a solution of (5α-cholestan-3β-yl)cyclopentadiene (3β-**3**) (5.6 g, 12.7 mmol) in 100 ml of ether at 0°C was added a solution of butyl lithium in hexane (8 ml, 1.6 M, 12.7 mmol). After stirring for 2 h at room temperature a white precipitate was formed. The cyclopentadienyllithium compound (3β-**4**) was collected by filtration and dried in vacuo; yield 4.3 g (76%).

3.11. Preparation of (5α-cholestan-3α-yl)cyclopentadienyllithium (3α-4)

Performed analogously the reaction of 3α-**3** with butyl lithium in ether/hexane gave 3α-**4** in 98% yield. ^{1}H NMR ([d_6]benzene/[d_8]tetrahydrofuran, 4:1) δ = 6.12–6.07 (m, 2H, Cp–H), 6.06–6.04 (m, 2H, Cp–H), 3.53–3.50 (m, 1H, cholestanyl-3-H), 2.10–0.50 (m, 46H, cholestanyl–H).

3.12. Preparation of (3β-methyl-5α-cholestan-3α-yl)cyclopentadienyllithium 9

As described for (3β-**4**) the reaction of **8** with butyl lithium gave **9** in 93% yield. ^{1}H NMR ([d_6]benzene/[d_8]tetrahydrofuran): δ = 5.79 (bs, 4H, Cp–H), 1.24 (s, 3H, 28-H), 0.92 (d, 3H, ^3J = 6.3 Hz, 21-H), 0.87 (s, 3H, 19-H), 0.84 (d, 6H, ^3J = 6.6 Hz, 26-H/27-H), 0.64 (s, 3H, 18-H), 2.1–0.5 (m, 27H, cholestanyl-H). ^{13}C NMR ([d_6]benzene/[d_8]tetrahydrofuran): δ = 38.5 (C-28), 22.9, 22.7, 18.9, 12.4, 12.3 (cholestanyl-CH_3), 43.0, 40.6, 39.9, 39.9, 36.7, 36.2, 35.7, 32.5, 29.6, 28.7, 24.6, 24.4, 21.4 (cholestanyl-CH_2), 101.9, 101.5 (Cp), 57.0, 56.9, 54.3, 42.4, 36.3, 36.0, 28.4 (cholestanyl-CH), 121.0 (*ipso*-C, Cp), 36.4, 25.0, 24.7 (cholestanyl-C).

3.13. Preparation of dichlorobis[η^5-(5α-cholestan-3β-yl)cyclopentadienyl]zirconium (3β-5)

To a suspension of 1.87 g (5.0 mmol) of $ZrCl_4(THF)_2$ in 20 ml of toluene was added at −78°C a suspension of 4.4 g (10 mmol) of the cyclopentadienyllithium reagent (3β-**4**) in 250 ml of tetrahydrofuran. The reaction mixture was kept at room temperature for 72 h. During this time a brown precipitate was formed. The resulting mixture was then stripped in vacuo and extracted with 200 ml of methylene chloride. After concentration of the combined extracts the residue was washed twice with pentane. After removal of the solvent in vacuo the organometallic product (3β-**5**) was recovered in 38% yield (2.0 g), m.p. 281°C dec. ^{1}H NMR ([d_6]benzene): δ 6.10–6.04 (m, 2H, Cp–H), 5.87–5.79 (m, 2H, Cp–H), 3.12–2.90 (m, 1H, 3-H), 2.08–0.57 (m, 92H, cholestanyl-H). ^{13}C NMR ([d_6]-benzene): δ = 12.1, 12.4, 18.7, 22.6, 22.8 (cholestanyl-CH_3), 21.0, 23.8, 24.2, 28.3, 28.9, 29.0, 32.1, 35.7, 36.2, 38.4, 39.5, 40.1 (cholestanyl-CH_2), 28.0, 35.6, 38.5, 46.4, 54.5, 56.3, 56.5 (cholestanyl–CH), 112.0, 112.2, 114.5 (double intensity, Cp), 35.8, 42.6 (cholestanyl–C), 140.7 (*ipso*-C, Cp), one signal (CH_2) of the cholestanyl substituent was not detected. IR (KBr): $\tilde{\nu}$ = 807, 816, 1025, 1037, 1057, 1095, 1262, 1384, 1445, 1460, 1467, 2851,

2867, 2929, 3168 cm^{-1}. Anal. Calcd. for $C_{64}H_{102}$ (M = 1030.6) C 74.37, H 9.95; found C 70.46, H 9.88%.

3.14. Preparation of dichlorobis[η^5-(5α-cholestan-3α-yl)cyclopentadienyl]zirconium (3α-5)

As described for compound (3β-**5**) the analogous reaction of 2.77 g (6.25 mmol) of the cyclopentadienyllithium reagent 3α-**4** in 100 ml of tetrahydrofuran with 1.2 g (3.25 mmol) of $ZrCl_4(THF)_2$ gave the organometallic product 3α-**5**. This compound was only observed in a ^1H NMR sample, attempts at further purification not being successful. ^1H NMR ([d_6]benzene): δ = 6.37–6.32 (m, 4H, Cp-H), 5.96–5.91 (m, 2H, Cp–H), 5.78–5.72 (m, 2H, Cp–H), 2.51–2.49 (m, 2H, cholestanyl-3'H), 2.2–0.6 (m, 92H, cholestanyl-H).

3.15. Preparation of dichlorobis[η^5-(3β-methyl-5α-cholestan-3α-yl)cyclopentadienyl]titanium (11a)

To a suspension of the cyclopentadienyllithium **9** (200 mg, 0.44 mmol) in toluene (20 ml) at −78°C was added 0.24 ml (42 mg, 0.22 mmol) of $TiCl_4$. The reaction mixture turned orange immediately. After stirring at −78°C for 30 min the reaction mixture was allowed to warm to room temperature and then stirred for another 5 h. For completion of the reaction the reaction mixture was heated to 60°C during 3 h. After cooling to room temperature the reaction mixture was filtered and stripped in vacuo. To the oily residue was added 5 ml of pentane. After stirring the organometallic complex **11a** precipitated as a red solid in 63% yield (140 mg), m.p. 209°C dec. ^1H NMR ($CDCl_3$): δ = 6.64–6.57 (m, 4H, Cp–H), 6.51–6.44 (m, 2H, Cp–H), 6.38–6.30 (m, 2H, Cp–H), 1.30 (s, 6H, 28-CH_3), 0.87 (d, 6H, ^3J = 5.3 Hz, 21-H), 0.84 (d, 12H, ^3J = 6.2 Hz, 26-H/27-H), 0.75 g (s, 6H, 19-H), 0.61 (s, 6H, 18-H), 2.30–0.61 (m, 62H, cholestanyl-H). ^{13}C NMR ([d_2] dichloromethane): δ = 146.3 (*ipso*-C, Cp), 124.1, 124.0, 117.6, 114.8 (Cp), 57.0, 56.8, 55.0, 54.4, 44.1, 43.0, 42.6, 40.5, 39.9, 38.0, 36.6, 36.2, 35.9, 35.3, 32.8, 32.4, 29.1, 28.6, 28.4, 24.5, 24.2, 22.9, 22.7, 21.4, 21.3, 18.9, 12.3, 12.2 (56C, cholestanyl). IR (KBr): $\tilde{\nu}$ = 803, 866, 1021, 1098, 1261, 1364, 1375, 1382, 1448, 1456, 1467, 2865, 2957, 3078 cm^{-1}. Anal. calcd. for $C_{66}H_{106}Ti$ (M = 1018.4) C 77.84, H 10.49; found C 76.58, H 10.50%.

3.16. Preparation of dichlorobis[η^5-(3β-methyl-5α-cholestan-3α-yl)cyclopentadienyl]zirconium (11b)

To a suspension of 0.31 g (0.82 mmol) of $ZrCl_4(THF)_2$ in 10 ml of toluene was added a suspension of 0.75 g (1.64 mmol) of the cyclopentadienyllithium reagent **9** in 20 ml of tetrahydrofuran at −78°C. The reaction mixture was kept at room temperature for 12 h. To complete the reaction the mixture was then heated to reflux for 6 h. During this time a white precipitate formed. The resulting mixture was then stripped in vacuo and extracted with 50 ml of methylene chloride to remove the precipitated lithium chloride. The clear filtrate was cooled to −30°C. Complex **11b** precipitated as a white solid and was collected by filtration. After removal of the solvents in vacuo the organometallic product **11b** was recovered in 71% yield (0.62 g), m.p. 256°C dec. ^1H NMR ([d_6]benzene): δ = 6.46–6.38 (m, 4H, Cp–H), 5.96–5.88 (m, 2H, Cp–H), 5.26–5.19 (m, 2H, Cp–H), 1.61 (s, 6H, 28-CH_3), 1.01 (d, 6H, ^3J = 6.5 Hz, 21-H), 0.93 (d, 12H, ^3J = 6.5 Hz, 26-H/27-H), 0.75 (s, 6H, 19-H), 0.67 (s, 6H, 18-H), 2.51–0.65 (m, 62H, cholestanyl–H). ^{13}C NMR ([d_6]-benzene): δ = 33.2, 22.9, 22.5, 18.7, 12.1, 12.0 (cholestanyl–CH_3), 43.8, 40.0, 39.5, 36.2, 35.4, 34.9, 31.9, 28.6, 28.2, 24.2, 23.9, 20.9 (cholestanyl–CH_2), 119.4, 119.2, 111.8, 109.6 (Cp), 56.5, 56.4, 54.6, 42.0, 35.8, 35.4, 28.0 (cholestanyl–CH), 140.9 (*ipso*-C, Cp), 42.6, 36.8, 35.8 (cholestanyl–C). IR (KBr): $\tilde{\nu}$ = 687, 813, 819, 830, 881, 1044, 1051, 1168, 1302, 1333, 1365, 1382, 1451, 1465, 1476, 2888, 2892, 2925, 2933, 3061 cm^{-1}. Anal. calcd. for $C_{66}H_{106}Zr$ (M = 1063.7) C 74.67, H 10.06; found C 73.90, H 10.34%.

3.17. Preparation of dichlorobis[η^5-(3β-methyl-5α-cholestan-3α-yl)cyclopentadienyl]hafnium (11c)

As described for compound **11b** the organometallic complex **11c** was obtained from 0.70 g (1.53 mmol) of cyclopentadienyllithium **9** and 0.25 g (0.77 mmol) of $HfCl_4$ in 45% yield (0.39 g) as a white solid, m.p. 215°C dec. ^1H NMR ([d_6]benzene): δ = 6.29–6.21 (m, 4H, Cp–H), 5.99–5.84 (m, 2H, Cp–H), 5.72–5.65 (m, 2H, Cp–H), 1.59 (s, 6H, 28-CH_3), 1.01 (d, 6H, ^3J = 6.3 Hz, 21-H), 0.93 (d, 12H, ^3J = 6.5 Hz, 26-H/27-H), 0.76 (s, 6H, 19-H), 0.67 (s, 6H, 18-H), 2.41–0.65 (m, 62H, cholestanyl–H). ^{13}C NMR ($CDCl_3$): δ = 33.2, 22.8, 22.6, 18.7, 12.2, 12.1 (cholestanyl–CH_3), 44.0, 40.0, 39.5, 36.2, 35.4, 35.0, 32.0, 28.7, 28.3, 24.2, 23.9, 20.9 (cholestanyl–CH_2), 117.9, 117.7, 112.7, 110.9 (Cp), 56.5, 56.3, 54.6, 42.0, 35.8, 35.4, 28.0 (cholestanyl–CH), 138.6 (*ipso*-C, Cp), 42.6, 36.6, 35.6 (cholestanyl–C). IR (KBr): $\tilde{\nu}$ = 734, 814, 823, 832, 1045, 1051, 1120, 1168, 1365, 1382, 1451, 1466, 1476, 2849, 2928, 3082 cm^{-1}. Anal. calcd. for $C_{66}H_{106}Hf$ (M = 1151.0) C 68.99, H 9.30; found C 68.62, H 9.56%.

3.18. Preparation of dichloro[η^5-(3β-methyl-5α-cholestan-3α-yl)cyclopentadienyl]cyclopentadienylzirconium (10)

To a suspension of cyclopentadienylzirconiumtrichloride (287 mg, 1.09 mmol) in 10 ml of toluene at

−78°C was added a solution of **9** (500 mg, 1.09 mmol) in 40 ml of tetrahydrofuran. The reaction mixture was allowed to warm to room temperature and stirred for 48 h. For completion of the reaction, the mixture was heated for 1 h to 60°C. The resulting mixture was then stripped in vacuo and extracted with 20 ml of dichloromethane. To remove the precipitated lithium chloride, the resulting suspension was filtered. The solution was reduced in vacuo to about 5 ml, from which a brown solid precipitated at −30°C, m.p. 256°C dec. ^{1}H NMR ([d_6]benzene): δ = 6.29–6.18 (m, 2H, Cp–H), 5.98 (s, 5H, Cp–H), 5.88–5.81 (m, 1H, Cp–H), 5.23–5.15 (m, 1H, Cp–H), 1.45 (s, 3H, 28-CH_3), 1.01 (d, 3H, ^3J = 6.4 Hz, 21-H), 0.92 (d, 6H, ^3J = 6.5 Hz, 26-H/27-H), 0.74 (s, 3H, 19-H), 0.65 (s, 3H, 18-H), 2.32–0.45 (m, 31H, cholestanyl–H). ^{13}C NMR ([d_6]benzene): δ = 33.6, 23.0, 22.8, 19.0, 12.3, 12.3 (cholestanyl–CH_3), 44.1, 40.3, 39.9, 36.7, 35.8, 35.1, 32.2, 29.0, 28.6, 24.4, 24.4, 21.3 (cholestanyl–CH_2), 118.5, 115.8, 112.5, 110.4 (Cp), 56.7, 56.6, 54.8, 42.4, 36.2, 35.7, 28.4 (cholestanyl–CH), 141.4 (*ipso*-C, Cp), 42.9, 36.9, 35.7 (cholestanyl–C). IR (KBr): $\tilde{\nu}$ = 687, 813, 819, 830, 881, 1044, 1051, 1168, 1302, 1333, 1365, 1382, 1451, 1465, 1476, 2888, 2892, 2925, 2933, 3085 cm^{-1}. Anal. calcd. for $C_{38}H_{58}Zr$ (M = 677.0) C 67.42, H 8.64; found C 67.52, H 7.97%.

3.19. Preparation of dimethylbis[η^5-(3β-methyl-5α-cholestan-3α-yl)cyclopentadienyl]zirconium (12b)

To a solution of the organometallic complex **11b** (0.25 g, 0.24 mmol) in 25 ml of toluene at −78°C was added 0.44 ml of a solution of methyl lithium in ether (1.6 M, 0.10 mmol). During 6 h the reaction mixture was warmed to room temperature and then stirred for another 12 h. Precipitated lithium chloride was removed by filtration, the resulting solution concentrated in vacuo to about 5 ml. The white complex **12b** precipitated at −30°C in 45% yield (0.11 g), m.p. 102°C dec. ^{1}H NMR ([d_6]benzene): δ = 6.19–6.11 (m, 2H, Cp–H), 6.02–5.95 (m, 2H, Cp–H), 5.95–5.88 (m, 2H, Cp–H), 5.83–5.74 (m, 2H, Cp–H), 1.11 (s, 6H, 28-CH_3), 0.96 (d, 6H, ^3J = 6.5 Hz, 21-H), 0.87 (d, 12H, ^3J = 6.4 Hz, 26-H/27-H), 0.74 (s, 6H, 19-H), 0.62 (s, 6H, 18-H), 2.10–0.61 (m, 62H, cholestanyl–H), 0.13 (s, 6H, Zr–CH_3). ^{13}C NMR ([d_8]toluene): δ = 111.6, 110.4, 109.4, 108.3 (Cp), 56.7, 56.6, 54.9, 42.3, 35.8, 28.5, 23.0, 22.8, 19.1, 12.3, 12.3 (cholestanyl–CH and CH_3), 34.0, 31.2 (Zr–CH_3), 134.2 (Cp), 44.8, 42.9, 40.4, 40.1, 36.8, 36.4, 36.0, 35.8, 32.3, 30.3, 29.3, 28.7, 28.5, 24.4, 21.5 (*ipso*-C, cholestanyl-CH_2), one CH/CH_3-group was not detected. IR (KBr): $\tilde{\nu}$ = 803, 1025, 1042, 1071, 1100, 1261, 1364, 1382, 1447, 1466, 2851, 2865, 2928, 2942, 2948, 3132 cm^{-1}. Anal. calcd. for $C_{68}H_{112}Zr$ (M = 1020.9) C 80.01, H 11.06; found C 78.30, H 10.78%.

3.20. Preparation of dimethylbis[η^5-(3β-methyl-5α-cholestan-3α-yl)cyclopentadienyl]hafnium (12c)

As described for complex **12b** the analogous reaction of **11c** (150 mg, 0.13 mmol) with methyl lithium (0.24 ml, 1.6 M in ether, 0.39 mmol) gave 91 mg of **12c** (63% yield), m.p. 184°C dec. ^{1}H NMR ([d_6]benzene): δ = 6.11–6.02 (m, 2H, Cp–H), 5.94–5.82 (m, 4H, Cp–H), 5.75–5.68 (m, 2H, Cp–H), 1.14 (s, 6H, 28-CH_3), 1.02 (d, 6H, ^3J = 6.4 Hz, 21-H), 0.93 (d, 12H, ^3J = 6.5 Hz, 26-H/27-H), 0.80 (s, 6H, 19-H), 0.69 (s, 6H, 18-H), 2.15–0.65 (m, cholestanyl–H), − 0.04 (s, 6H, Hf–CH_3). ^{13}C NMR ([d_8]toluene): δ = 111.4, 109.9, 109.1, 107.4 (Cp), 56.7, 56.6, 54.9, 42.3, 37.5, 36.3, 28.5, 23.0, 22.8, 19.1, 12.4, 12.4 (cholestanyl–CH and CH_3), 35.8, 33.8 (Hf–CH_3), 135.6 (Cp), 45.0, 42.9, 40.4, 40.1, 36.8, 36.1, 36.0, 35.7, 32.3, 30.3, 29.3, 28.7, 24.5, 21.4 (cholestanyl–CH_2 and C), one CH_2/C-group was not detected. IR (KBr): $\tilde{\nu}$ = 461, 803, 877, 1054, 1365, 1382, 1448, 1466, 2849, 2865, 2927, 2946, 3089 cm^{-1}. Anal. calcd. for $C_{68}H_{112}Zr$ (M = 1020.9) C 80.01, H 11.06; found C 78.30, H 10.78%.

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