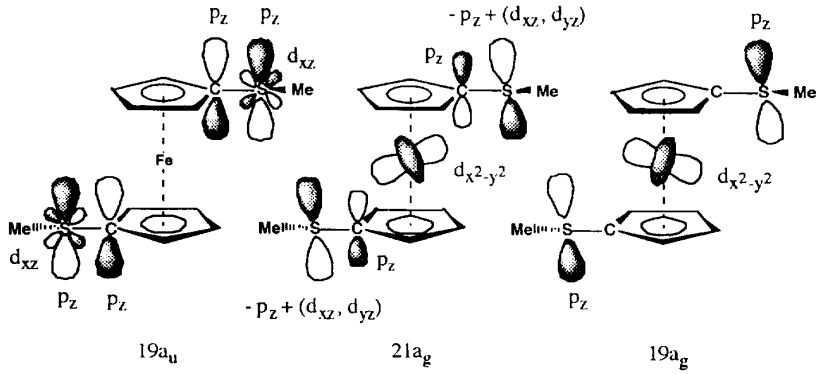

Fig 3. Stages of selected molecular orbitals for $(C_5H_4SMe)_2Fe$.

In the case of group 4 bent metallocenes the effect of the sulfur-based substituent, its electron-withdrawing action, is similar to the substituted ferrocene. However, because of the geometric requirements (bent versus parallel metallocene), the through-space sulfur-metal interaction should vanish. The sulfur-metal(IV) distances would then be longer than the sulfur-iron ones. Consequently, the properties of the bent metallocenes will be discussed only on the basis of electrochemical and ^{13}C NMR results without molecular orbital studies.

In THF, all the bent metallocene complexes **4**–**6** display a similar redox behavior in that the first anodic process is reversible for **5** and **6** [12a] and pseudo-reversible for **4** [12b,c]. The $E_{1/2}$ values obtained under argon atmosphere are reported in table I.

According to data on the electrochemical behavior of bent complexes [12d], the variation of the $E_{1/2}$ values as a function of the metal is linear with respect to the variation of ionization potentials. For both Cp_2MCl_2 and $(C_5H_4SCH_2CH_2CH_3)_2MCl_2$ series, the $E_{1/2}$ values increase with an increase in the ionization potentials.

Electrochemical data (table I) suggest that with respect to the unsubstituted Cp_2MCl_2 (M = Ti, Zr and Hf) complexes, the sulfur-based substituent draws away some of the electron density from the metal center and this effect increases significantly in the sequence Ti < Zr ~ Hf. This may be due to a different contribution of metal orbitals to the redox orbitals of complexes.

Another approach for checking the relative electron density at the metal centers is the observation of the C-H coupling constants of methyl groups in $Cp'_2M(CH_3)_2$ [13, 14]. An increase in electron density at the metal center causes a lowering of the J_{CH} of the methyl groups directly bound to the metal while a decrease of electron density increases J_{CH}. The J_{CH} values for $Cp_2M(CH_3)_2$ and $(C_5H_4SCH_2CH_2CH_3)_2M(CH_3)_2$ are reported in the *Experimental section*. An increase of 0.7–0.8 Hz in J_{CH} values is observed upon the substitution of propylthio group for a hydrogen atom. Thus, similar effects of electrochemical behavior of propylthio-complexes **4**–**6** and of ^{13}C NMR coupling constants in dimethyl derivatives are observed.

Chemical shifts of cyclopentadienyl carbon atoms in ^{13}C NMR resonances may also give an insight into the relative electron densities retained on rings. As expected, these resonances move upfield on going from titanium to hafnium complexes (table I). This is due to the effect of neighboring atoms via a non-local diamagnetic contribution to the overall shielding [15]. In substituted compounds, the carbon atoms are slightly deshielded with respect to the non-substituted ones. As in the case of ferrocenes this observation may be ascribed to the electron-withdrawing property of the propylthio group. The effects are slightly stronger in the Zr and Hf derivatives than in the Ti ones (deshieldings by 2.4, 2.5 and 2.0 ppm, respectively). It has been suggested, however, that smaller metals cause the steric effects to be more pronounced [16]. Thus, the differences of electrochemical and magnetic behavior observed between titanium and zirconium and hafnium complexes are of electronic nature.

Description of the structure of 5

The crystal structure of **5** is built of discrete $(C_5H_4SCH_2CH_2CH_3)_2ZrCl_2$ molecules. They exhibit a pseudotetrahedral geometry typical of bent zirconocenes bearing two ligands in the plane bisecting those of C_5H_4S rings (fig 4). The metric parameters (table III) involving the Zr-Cp and Zr-Cl vectors fall well within the range generally observed for this class of compounds [17]. An interesting feature of the molecular structure of **5** consists of the relative orientation of S^nPr substituents on two Cp rings. This conformation may be deduced from the value of torsion angle S1, C1, Cp1, Cp2/Cp1, Cp2, C1*, S1* which is close to 20°. For the non-substituted bent metallocenes when this angle is 0° the conformation is eclipsed, whereas 36° corresponds to the staggered conformation. Thus, the conformation of Cp rings in **5** is intermediate, with the thiolates symmetrically displayed with respect to the Cp1/Zr/Cp2 plane and close to this plane. In the presence of bulkier substituents like *t*-Bu, the conformational torsion angle may be very large reaching 180°. This observation indicates that the actual conformation in substituted bent metallocenes is primarily governed by the repulsions between the substituents on Cp rings and the ligands present in the bisecting plane, and not by the repulsions between the substituents alone.

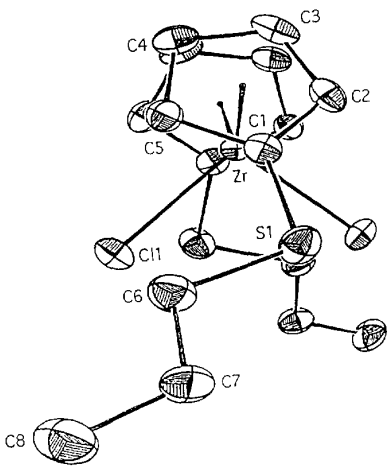

Fig 4. ORTEP drawing (50% probability level) of $(C_5H_4SCH_2CH_2CH_3)_2ZrCl_2$ **5**. Selected distances and angles: Zr-Cl: 2.447(1) Å; Zr-Cp: 2.214 Å; Cl-Zr-Cl: 96.5(1) Å; Cp-Zr-Cp: 130.3 Å.

Table III. Crystallographic data for $(C_5H_4SCH_2CH_2CH_3)_2ZrCl_2$ **5**.

Molecular formula	$ZrCl_2S_2C_{16}H_{22}$
Formula weight, g.mol^{-1}	440.61
Crystal size (mm)	0.3 × 0.3 × 0.3
Crystal system	Orthorhombic
Space group	*Pbcn* (No 60)
Cell dimensions	
a, (Å)	11.943(1)
b, (Å)	6.883(2)
c, (Å)	22.412(2)
V, (Å^3)	1842.4(2)
Z	4
ρ_{calc} (g.cm^{-3})	1.588
F(000)	896
Linear absorption (μ, cm^{-1})	10.897
Radiation (Å)	λ (Mo$K\alpha$) 0.71073
θ range (°)	2–25
Scan type	$\omega - 2\theta$
Scan width (°)	$\Delta\omega = 0.81 + 0.347 \tan\theta$
No of reflections measured	2187
Temperature (K)	296(1)
Decay (%)	−6.5, corrected
Cut off for observed data	$I \geqslant 3\sigma(I)$
No of unique observed data (NO)	1302
No of variables (NV)	129
R(*F*)	0.027
*R*w(*F*)	0.027
Weight,	
$w^{-1} = [\sigma^2(I) + (pF_o^2)^2]^{1/2}$, *p*	0.040
GOF	0.446
ρ_{max}/ρ_{min} (e$^-$/Å^3)	0.32/−0.26

Experimental section

General considerations

Except where otherwise indicated, all manipulations were carried out under argon using standard Schlenk techniques. Solvents were dried by distillation over appropriate drying agents. Propyl disulfide was obtained from Fluka Chemika, distilled under vacuum and stored under argon. Sodium hydride (50% oil dispersion, Aldrich Chemical) was washed with hexane and stored under argon. Zirconium tetrachloride, from Merck, was sublimed before storage under argon. $TiCl_3$·3THF [18], $CpTiCl_3$ [19], $CpZrCl_3$,DME [20] were prepared according to published methods. For Fe_2Cl_4·3THF, a modification of the published method [21] was used: 5 g of $FeCl_2$ was refluxed in 90 mL of THF for 45 min, the brown solvent was then changed, and the procedure repeated until the solvent remained colorless. Finally, 5 g (30%) of a light-brown solid, very sensitive to moisture was obtained and stored under argon. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200 instrument in C_6D_6 (^{1}H) and $CDCl_3$ (^{13}C) at room temperature, if not stated otherwise, and were referenced internally using the residual solvent resonances relative to tetramethylsilane (δ = 0 ppm). For the multiplicity of the signal, 'pt' means pseudo-triplet and 'sx' means sextet. Mass spectra were obtained by a Kratos concept IS spectrometer operating at 70 eV. Melting points were determined with a Kofler apparatus. Elemental analyses were performed by the Service central d'analyses du CNRS, Vernaison.

Table IV. Positional parameters of non-hydrogen atoms for $(C_5H_4SCH_2CH_2CH_3)_2ZrCl_2$ **5**.

Atom	x	y	z	B (*Å^2*)
Zr	0.5	0.19865(6)	0.75	2.405(7)
Cp	0.4798	0.3337	0.6610	
Cl	0.65172(8)	−0.0381(1)	0.73984(4)	3.86(2)
S1	0.42843(9)	−0.0389(2)	0.60128(4)	4.22(2)
C1	0.4616(3)	0.1813(5)	0.6370(1)	3.06(6)
C2	0.3813(3)	0.3059(6)	0.6627(2)	3.75(8)
C3	0.4373(4)	0.4692(5)	0.6851(2)	4.10(8)
C4	0.5518(4)	0.4449(5)	0.6751(2)	3.77(8)
C5	0.5671(3)	0.2676(5)	0.6452(1)	3.18(7)
C6	0.5646(4)	−0.1157(6)	0.5750(2)	4.32(9)
C7	0.5531(4)	−0.2949(6)	0.5365(2)	4.33(9)
C8	0.6662(4)	−0.3681(7)	0.5166(2)	6.9(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) * [a^2 * B(1,1) + b^2 * B(2,2) + c^2 * B(3,3) + ab(\cos\gamma) * B(1,2) + ac(\cos\beta) * B(1,3) + bc(\cos\alpha) * B(2,3)]$.

Synthesis of $C_5H_5SCH_2CH_2CH_3$ **1** *and $C_5H_4SCH_2CH_2CH_3Na$* **2**

To a solution of cyclopentadienyllithium (2.63 g, 36.5 mmol) in 45 mL THF was added dropwise 5.7 mL (36.5 mmol) of propyl disulfide. The resulting mixture was stirred for 4 h to produce a salmon-pink limpid solution. The solvent was removed under reduced pressure and the white residue was washed with 5 mL pentane. The latter residue was extracted with diethyl ether (20 mL, 5 mL, then 5 mL) to give a light-yellow solution. After removal of the solvent, a brown oil (**1**) resulted which was dissolved in 15 mL THF·NaH (0.84 g, 36.5 mmol) was added and the mixture was stirred for 2 h. The excess of NaH was removed by filtration, washed by THF (2 × 5 mL) and the filtrate evaporated. The crude product was washed with diethyl ether to give a white solid (**2**, 0.3 g, 4%).

At −50 °C, a solution of propyl disulfide (1.33 mL, 8.4 mmol) and three drops of triethylamine in 20 mL dichloromethane was slowly added (2 h) to a solution of sulfuryl chloride (0.68 mL, 8.4 mmol) in 20 mL dichloromethane. When the addition was finished the reaction mixture was slowly warmed to room temperature

giving a yellow solution. The solvent was removed under reduced pressure. The yellow liquid residue was diluted with 20 mL THF and slowly added to a cold solution (−50 °C) of cyclopentadienyllithium (1.22 g, 16.8 mmol) in 20 mL THF. The red brown reaction mixture was left to warm to room temperature. The solvent was removed under reduced pressure and the residue was extracted which diethyl ether (3 × 10 mL). The solvent was again removed yielding **1**, then 25 mL THF, followed by NaH (0.4 g, 16.8 mmol) were added. The mixture was stirred for 2 h. The excess of NaH was removed by filtration, washed by THF (2 × 5 mL) to give a deep purple solution. The solvent was removed and the residue was washed by diethyl ether affording a white solid **2** (1.19 g, 40%).

For **2**: ^{1}H NMR, δ (ppm), THF-d_8: 0.88 (t, CH_3, J = 7.2 Hz), 1.47 (sx, CH_2, J = 7.2 Hz), 2.30 (t, SCH_2, J = 7.2 Hz), 5.68 (pt, H_α, J = 2.6 Hz), 5.80 (pt, H_β, J = 2.7 Hz).

^{13}C NMR: 13.5 (CH_3), 23.5 (CH_2), 42.5 (SCH_2), 102.7 (C_1), 104.9 ($C_{2,5}$), 111.7 ($C_{3,4}$).

Synthesis of $(C_5H_4SCH_2CH_2CH_3)_2Fe$ **3**

To a suspension of Fe_2Cl_4·3THF (0.861 g, 1.83 mmol) in 15 mL THF, cooled to 0 °C, was added a solution of (propylthio)cyclopentadienylsodium **2** (1.19 g, 7.33 mmol) in 15 mL THF. The resulting suspension was stirred for 2 h to give a brown mixture. The solvent was removed under reduced pressure and replaced by diethyl ether (30 mL). The mixture was then treated with water and the organic layer collected. The water layer was extracted with diethyl ether and the combined organic extracts were washed with water before being dried over $MgSO_4$. After filtration, the solvent was removed to give a red oil. $(C_5H_4SCH_2CH_2CH_3)_2Fe$ **3** was separated, as a red oily product, by chromatography using toluene as eluent.

^{1}H NMR, δ (ppm): 0.80 (t, CH_3, J = 7.3 Hz), 1.45 (sx, CH_2, J = 7.3 Hz), 2.43 (t, SCH_2, J = 7.3 Hz), 4.06 (pt, H_β, J = 2.0 Hz), 4.30 (pt, H_α, J = 1.8 Hz).

^{13}C NMR, δ (ppm): 13.9 (CH_3), 23.7 (CH_2), 40.2 (SCH_2), 71.3 ($C_{3,4}$), 75.4 ($C_{2,5}$), 81.9 (C_1).

MS, m/z (fragment, relative intensity): 384 (M^+, 100), 291 ($M^+ - C_3H_7$, 20), 258 ($M^+ - C_3H_7SH$, 270), 249 ($(C_5H_4SH)_2Fe^+$, 50), 226 ($C_{13}H_{16}Fe^+$, 32), 218 ($C_{10}H_{10}SFe^+$, 50), 195 ($C_8H_{11}SFe^+$, 46), 184 ($C_{10}H_8Fe^+$, 20), 161 ($C_8H_9Fe^+$, 60), 152 ($C_5H_4SFe^+$, 70), 121 ($C_5H_5Fe^+$, 35), 97 ($C_5H_5S^+$, 70).

Synthesis of $(C_5H_4SCH_2CH_2CH_3)_2TiCl_2$ **4**

To a mixture of $TiCl_3$·3THF (1.14 g, 3.08 mmol) in 30 mL THF was added a solution of 1.01 g (6.22 mmol) of (propylthio)cyclopentadienylsodium **2** in 20 mL THF. The reaction solution was stirred for 5 h to give a brown mixture. Carbon tetrachloride (20 mL) was added to oxidize Ti(III) species, and the mixture became red brown. The solvents were removed under reduced pressure and recrystallization from hexane gave green powder (0.46 g, 37%) of **4**, mp 79 °C.

^{1}H NMR, δ (ppm): 0.76 (t, CH_3, J = 7.3 Hz), 1.41 (sx, CH_2, J = 7.3 Hz), 2.72 (t, SCH_2, J = 7.3 Hz), 6.01 (m, H_β), 6.06 (m, H_α).

^{13}C NMR, δ (ppm): 14.1 (CH_3), 23.0 (CH_2), 36.3 (SCH_2), 119.5 ($C_{3,4}$), 120.7 ($C_{2,5}$), 133.9 (C_1).

MS, m/z (fragment, relative intensity): 396 (M^+, 25), 257 ($M^+ - C_5H_4SCH_2CH_2CH_3$, 60), 179 ($C_5H_4SClTi^+$, 30), 139 ($C_5H_4SCH_2CH_2CH_3^+$, 100), 97 ($C_5H_5S^+$, 60).

Anal calc for $C_{16}H_{22}Cl_2S_2Ti$: C, 48.37; H, 5.58; S, 16.14. Found: C,48.13; H, 5.55; S, 14.62.

Synthesis of $(C_5H_4SCH_2CH_2CH_3)_2ZrCl_2$ **5**

At −20 °C, a solution of 1.09 g (6.72 mmol) of (propylthio)-cyclopentadienylsodium **2** in 20 mL THF was added to a mixture of $ZrCl_4$ (0.8 g, 3.43 mmol) in 20 mL THF. When the addition was finished, the reaction mixture was left to warm at ambient conditions. The yellow solution was filtered and the white precipitate eliminated. The solvent was removed and the residue was recrystallized from hexane to give yellow needles (0.74 g, 49%) of **5**, mp 69 °C.

^{1}H NMR, δ (ppm): 0.76 (t, CH_3, J = 7.3 Hz), 1.38 (sx, CH_2, J = 7.3 Hz), 2.60 (t, SCH_2, J = 7.3 Hz), 6.00 (pt, H_β, J = 2.8 Hz), 6.08 (pt, H_α, J = 2.8 Hz).

^{13}C NMR, δ (ppm): 14.0 (CH_3), 23.2 (CH_2), 37.6 (SCH_2), 116.5 ($C_{3,4}$), 118.5 ($C_{2,5}$), 125.5 (C_1).

MS, m/z (fragment, relative intensity): 438 (M^+, 55), 299 ($M^+ - C_5H_4SCH_2CH_2CH_3$, 100), 221 ($C_5H_4ClSZr^+$, 50), 139 ($C_5H_4SCH_2CH_2CH_3^+$, 12), 97 ($C_5H_5S^+$, 48).

Anal calc for $C_{16}H_{22}Cl_2S_2Zr$: C, 43.61; H, 5.03; S, 14.54. Found: C, 43.59; H, 5.05; S, 14.72.

Synthesis of $(C_5H_4SCH_2CH_2CH_3)_2HfCl_2$ **6**

The same experimental process as above, $HfCl_4$ (0.68 g, 2.12 mmol) in 30 mL THF and **2** (0.69 g, 4.25 mmol) in 20 mL THF afforded white needles (0.335 g, 30%) of **6**, mp 50 °C.

^{1}H NMR, δ (ppm): 0.76 (t, CH_3, J = 7.3 Hz), 1.37 (sx, CH_2, J = 7.3 Hz), 2.56 (t, SCH_2, J = 7.3 Hz), 5.94 (pt, H_β, J = 2.6 Hz), 6.05 (pt, H_α, J = 2.8 Hz).

^{13}C NMR, δ (ppm) : 14.0 (CH_3), 23.2 (CH_2), 37.8 (SCH_2), 114.9 ($C_{3,4}$), 118.0 ($C_{2,5}$), 122.7 (C_1).

MS, m/z (fragment, relative intensity): 528 (M^+, 65), 389 ($M^+ - C_5H_4SCH_2CH_2CH_3$, 100), 347 ($M^+ - C_5H_4SCH_2CH_2CH_3 - C_3H_6$, 52), 311 ($C_5H_4ClSHf^+$, 40), 139 ($C_5H_4SCH_2CH_2CH_3^+$, 10), 97 ($C_5H_5S^+$, 25).

Anal calc for $C_{16}H_{22}Cl_2S_2Hf$: C, 36.40; H, 4.21; S, 12.15. Found: C,36.32; H, 4.21; S, 12.02.

Synthesis of $(C_5H_5)(C_5H_4SCH_2CH_2CH_3)TiCl_2$ **7**

A solution of (propylthio)cyclopentadienylsodium **2** (0.67 g, 4.1 mmol) in 15 mL THF was added to a solution of 0.905 g (4.1 mmol) of $CpTiCl_3$ in 20 mL of THF to give a brown mixture which was stirred at room temperature for 12 h. The solvent was removed, the residue was purified by chromatography on silica with diethyl ether/toluene (1:1) as eluent and then recrystallized in hexane to give **7**, mp 75 °C, as green powder (0.3 g, 23%).

^{1}H NMR, δ (ppm): 0.75 (t, CH_3, J = 7.3 Hz), 1.38 (sx, CH_2, J = 7.3 Hz), 2.67 (t, SCH_2, J = 7.3 Hz), 5.87 (m, H_β), 5.97 (m, H_α), 6.05 (s, C_5H_5).

^{13}C NMR, δ (ppm) : 14.1 (CH_3), 23.0 (CH_2), 36.3 (SCH_2), 119.1 ($C_{3,4}$), 120.2 ($C_{2,5}$), 121.5 (C_5H_5), C_1 not observed.

MS, m/z (fragment, relative intensity): 322 (M^+, 15), 139 ($C_5H_4SCH_2CH_2CH_3^+$, 100), 97 ($C_5H_5S^+$, 70).

Anal calc for $C_{13}H_{16}Cl_2STi$: C, 48.32; H, 4.99. Found: C, 48.89; H, 5.46.

Synthesis of $(C_5H_5)(C_5H_4SCH_2CH_2CH_3)ZrCl_2$ **8**

At −30 °C, a solution of (propylthio)cyclopentadienyl-sodium **2** (0.54 g, 3.3 mmol) in 15 mL THF was added to a solution of $CpZrCl_3$·DME (1.17 g, 3.3 mmol) in 10 mL THF. The orange mixture was stirred 12 h at room temperature. The solvent was removed under reduced pressure, the product extracted with toluene and then recrystallized to give yellow crystals, mp 66 °C, (0.66 g, 55%) of **8**.

^{1}H NMR, δ (ppm): 0.76 (t, CH_3, J = 7.3 Hz), 1.36 (sx, CH_2, J = 7.3 Hz), 2.55 (t, SCH_2, J = 7.3 Hz), 5.89 (pt, H_β, J = 2.8 Hz), 5.96 (pt, H_α, J = 2.8 Hz), 6.05 (s, C_5H_5).

^{13}C NMR, δ (ppm): 14.0 (CH_3), 23.1 (CH_2), 37.6 (SCH_2), 116.2 ($C_{3,4}$), 118.1 ($C_{2,5}$), 117.3 (C_5H_5), 124.3 (C_1).

MS, m/z (fragment, relative intensity): 364 (M^+, 15), 299 ($M^+ - C_5H_5$, 20), 223 ($M^+ - C_5H_5 - C_3H_7SH$, 30), 139 ($C_5H_4SCH_2CH_2CH_3^+$, 70), 97 ($C_5H_5S^+$, 100).

Anal calc for $C_{13}H_{16}Cl_2SZr$: C, 42.60; H, 4.40; S, 8.74. Found: C,42.79; H, 4.46; S, 8.28.

Synthesis of $(C_5H_5)_2M(CH_3)_2$ [22] and $(C_5H_4SCH_2CH_2CH_3)_2M(CH_3)_2$ M = Ti, Zr, Hf

The aim of the procedure was not to isolate the dimethyl complexes but only to carry out ^{13}C NMR studies, especially to monitor the evolution of the C–H coupling constant of the methyl groups bonded directy to the metal.

To a suspension of about 0.1 g of dichloride precursors in diethyl ether at −70 °C was added two equivalents of methyllithium in diethyl ether. The mixture was then allowed to warm to room temperature. First the reaction mixture became limpid, and then a suspension of LiCl was formed. The solid was removed by filtration and the solvent evaporated under reduced pressure leading to a solid which was used for NMR studies.

- $(C_5H_5)_2M(CH_3)_2$

^{1}H NMR, δ (ppm): **M = Ti**, −0.07 (s, CH_3), 5.67 (s, C_5H_5); **M = Zr**, −0.37 (s, CH_3), 6.10 (s, C_5H_5); **M = Hf**, −0.58 (s, CH_3), 6.02 (s, C_5H_5). All values in accord with [22].

^{13}C NMR, δ (ppm): **M = Ti**, 46.0 (q, CH_3, J = 123.8 Hz), 113.5 (d, C_5H_5, J = 172.0 Hz); **M = Zr**, 30.3 (q, CH_3, J = 117.4 Hz), 110.8 (d, C_5H_5, J = 172.0 Hz); **M = Hf**, 36.5 (q, CH_3, J = 115.3 Hz), 110.4 (d, C_5H_5, J = 173.0 Hz).

- $(C_5H_4SCH_2CH_2CH_3)_2M(CH_3)_2$

^{1}H NMR, δ (ppm): **M = Ti**, −0.03 (s, CH_3), 1.01 (t, CH_3, J = 7.3 Hz), 1.69 (sx, CH_2, J = 7.3 Hz), 2.81 (t, SCH_2 J = 7.3 Hz), 5.93 (pt, H_β, J = 2.7 Hz), 6.08 (pt, H_α, J = 2.7 Hz); **M = Zr**, −0.31 (s, CH_3), 0.96 (t, CH_3, J = 7.3 Hz), 1.60 (sx, CH_2, J = 7.3 Hz), 2.71 (t, SCH_2 J = 7.3 Hz), 5.98 (pt, H_β, J = 2.7 Hz), 6.08 (pt, H_α, J = 2.7 Hz); **M = Hf**, −0.49 (s, CH_3), 0.97 (t, CH_3, J = 7.3 Hz), 1.60 (sx, CH_2, J = 7.3 Hz), 2.71 (t, SCH_2, J = 7.3 Hz), 5.93 (pt, H_β, J = 1.5 Hz), 6.08 (pt, H_α, J = 1.5 Hz).

^{13}C NMR, δ (ppm): **M = Ti**, 14.0 (q, CH_3, J = 124.9 Hz), 23.7 (t, CH_2, J = 126.4 Hz), 38.8 (t, SCH_2, J = 140.0 Hz), 47.7 (q, CH_3, 124.5 Hz), 113.4 (d, C_3, J = 173.0 Hz), 118.1 (d, C_2, J = 175.0 Hz), 120.6 (s, C_1); **M = Zr**, 13.9 (q, CH_3, J = 126.7 Hz), 23.5 (t, CH_2, J = 126.2 Hz), 31.9 (q, CH_3, J = 118.2 Hz), 39.2 (t, SCH_2, 136.0 Hz), 111.1 (d, C_3, J = 167.0 Hz), 115.3 (d, C_2, J = 173.0 Hz), 117.5 (s, C_1); **M = Hf**, 13.9 (q, CH_3, J = 125.8 Hz), 23.5 (t, CH_2, J = 129.0 Hz), 37.7 (q, CH_3, J = 116.0 Hz), 39.4 (t, SCH_2, 142.0 Hz), 110.6 (d, C_3, J = 168.0 Hz), 115.5 (d, C_2, J = 169.0 Hz), 116.3 (s, C_1).

X-ray analysis of $(C_5H_4SCH_2CH_2CH_3)_2ZrCl_2$ **5**

A yellow crystal of **5** grown from a solution in hexane was used for unit cell determination and data collection, carried out at 296(1) K on an Enraf-Nonius CAD4 diffractometer with Mo$K\alpha$ radiation (λ = 0.71073 Å). The pertinent crystallographic data are given in table IV. All calculations were carried out by use of the Molen package with neutral-atom scattering factors taken from the usual sources [23]. Intensities were corrected for Lorentz and polarization effects. Because of the low value of linear absorption coefficient no absorption correction was made. All non-hydrogen atoms could be easily located from three dimensional Patterson and subsequent difference Fourier maps. These atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in calculated positions (HYDRO) and included in the structure in a riding model with B_{iso} fixed at 1.3 B_{eq} for the carbon atoms bearing them. Very good residuals, estimated standard deviations of bond distances and angles as well as the final peaks on difference Fourier card confirm a good quality of the structure of **5**. Positional parameters of non-hydrogen atoms are given in table IV.

Electrochemistry

Tetrabutylammonium hexafluorophosphate, for electrochemical studies, obtained from Fluka Chemika was recrystallized twice from absolute alcohol, then vacuum dried at 100 °C, before being stored under argon. The cyclic voltammetry data were first collected using a Tacussel UAP4 unit, then recorded on a Nicolet 3091 Digital Oscillograph (Madisson, WI), and subsequently reproduced on an XY recorder (Sefram-TGM.164). The electrochemical experiments were carried out at room temperature, under argon atmosphere on a vacuum line in THF, CH_2Cl_2 or CH_3CN, with 0.5 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Three standard electrodes configuration was used, with a platinum disc working electrode (Ø = 0.8 mm), a platinum wire counter electrodes, and an $Ag/AgNO_3$ ($AgNO_3$: 0.01 M; Bu_4NPF_6: 0.2 M in CH_3CN) reference electrode. Before each experiment, the reference electrode was checked with an aqueous saturated calomel electrode.

Supplementary material

Anisotropic parameters of non-hydrogen atoms, positional parameters of hydrogen atoms, a full list of bond distances and angles and least-squares planes, stereoscopic view for molecular bending (5 pages). (F_o/F_c tables were submitted for the referee's use.) Supplementary material data have been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorshire, UK, as supplementary publication N° = SUP 90436 and is available on request from the Document Supply Center.

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Stereoselectivity in the template-directed synthesis of D_3 (chiral) and C_{3h} (achiral) cryptophanes with long $O(CH_2)_nO$ spacer bridges

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Summary — Cryptophanes are hollow molecules of nanometric size made of two cyclotriveratrylene units assembled in front of one another by three spacer bridges. In this paper, we focus on the synthesis and characterization of medium and large cryptophanes having $O(CH_2)_nO$ spacer bridges with n in the range 4–10. We show that the template method used for their synthesis affords mixtures of *anti* (racemic or resolved) and *syn* (achiral) stereomers, in a ratio depending on the even or odd parity of n. A similar even–odd dependence is observed in the magnitude of the rotation of the *anti* stereomers. For the largest members of the family ($n \geqslant 6$), we have evidenced the existence of in–out topoisomers slowly equilibrating with the out–out ones in solution at room temperature.

cryptophane / cyclotriveratrylene / stereochemistry / topoisomer / host–guest chemistry / template synthesis

Résumé — Étude de la stéréosélectivité dans la synthèse de cryptophanes D_3 (chiraux) et C_{3h} (achiraux) de grande taille par la méthode dite «template». *Les cryptophanes sont des molécules creuses de taille nanométrique constituées de deux unités cyclotrivératryléniques liées face à face par trois espaceurs. Dans cet article, nous examinons la synthèse de cryptophanes de taille moyenne à grande possédant des espaceurs $O(CH_2)_nO$ avec* n = *4–10. Nous montrons que la méthode dite «template» utilisée pour leur synthèse produit des mélanges de stéréoisomères* anti *(racémiques ou dédoublés) et* syn *(achiraux), dans un rapport dépendant de la parité de* n. *Cette parité de* n *influe également sur la valeur du pouvoir rotatoire de stéréoisomères* anti. *Pour les plus grands cryptophanes (*n $\geqslant$ *6) nous avons mis en évidence l'existence de topoisomères in–out en équilibre lent avec les formes out–out en solution à la température ambiante.*

cryptophane / cyclotrivératrylène / stéréochimie / topoisomère / chimie supramoléculaire

Introduction

The name *cryptophane* designates hollow molecules of nanometric size made of two cyclotriveratrylene (CTV) units assembled in front of one another by three spacer bridges (fig 1) [1–3]. Since their discovery in 1981 [4], these molecules have attracted interest in view of their ability to bind a variety of neutral and cationic species in the interior of their cavity. Due to the C_3 symmetry of their CTV caps, there exist two stereomeric cryptophane structures **1** (*anti*) and **2** (*syn*) differing from one another by the relative configurations (M or P) [5] of the caps which in turn determine the positioning of the R and R′ peripheral substituents with respect to the spacers. In the cryptophanes discussed in this paper, the three spacers of structure O(Z)O are identical (Z = $(CH_2)_n$) and the R and R′ peripheral substituents are methoxy groups; hence both stereomers have a north–south three-fold axis, the *anti* isomer being D_3 (chiral) and the *syn* C_{3h} (achiral). In the few reported instances where substituents R and R′ are different, both stereomers belong to the chiral C_3 point group. In cryptophanes **1** and **2** with $n \geqslant 3$, the existence of conformational isomers in which one CTV cap is turned inward can also be anticipated; these will hereafter be designated as in–out (1′ or 2′) topoisomers.

Host–guest studies have shown that *anti* cryptophanes with short (n = 2 or 3) or medium (n = 5) $O(CH_2)_nO$ spacer bridges bind a variety of roughly spherically shaped species including methane and chlorofluorocarbons [6], bromochlorofluoromethane (enantioselective binding [7]), isobutane [8], halogenomethanes [9–11], tetramethylpyrrolidine nitroxide radicals [12], and quaternary ammonium derivatives such as acetylcholine and congeners [13]. Almost nothing is known about the complexing properties of the corre-

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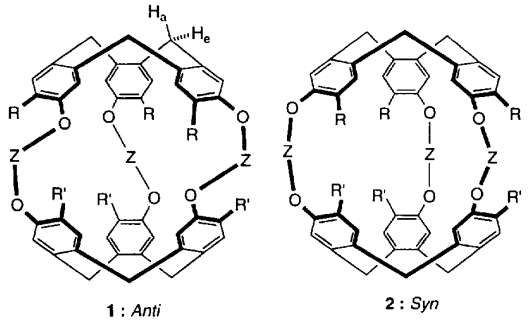


(-)-**1a-i** and **2a-i** : R = R' = OMe ; Z = $(CH_2)_n$ with n = 2-10

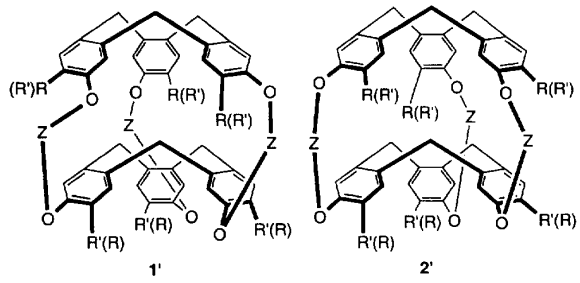


Fig 1. Cryptophane structures **1** and **2** and the corresponding in-out topoisomers **1'** and **2'**.

sponding *syn* stereomers, except in one case [14]. The *anti* and *syn* cryptophanes with $OCH_2C{\equiv}C{-}C{\equiv}CCH_2O$ bridges bind, inter alia, cubane, benzene, and propylene oxide [15]. Cryptophanes with $OCH_2CH{=}CHCH_2O$ and $OCH_2C{\equiv}CCH_2O$ bridges have also been synthesized [16, 17], but their complexing properties are still unknown. Recent experiments have shown that mixtures of isomers **1** and **2** with n = 9 and 10 form Langmuir monolayers at the air–water interface [18], and this finding may open new perspectives in the area of chemical sensors.

In this paper, we focus on the synthesis and characterization of medium and large cryptophanes with $O(CH_2)_nO$ bridges in the range n = 4–10. With the exception of cryptophane-O (**1d**), the conformational properties and host–guest chemistry of large cryptophanes are still unexplored.

There exist currently two main methods for the synthesis of cryptophanes. The *direct method* (fig 2(a), also called the *two-step method*) is simple and straightforward, but is in practice restricted to the preparation of the smallest members and specifically of *anti* stereomers with n = 3 (**1b**) and 5 (**1d**), in which the two CTV caps are identical [19]. The *template method* (fig 2(b)) is somewhat lengthier but is in principle more versatile. It allows access to cryptophanes provided with two CTV caps bearing identical [4] or different [9] peripheral substituents as well, and lends itself to the preparation of optically active cryptophanes starting from resolved CTV templates [17]. We report in this paper that the scope of the template method can be extended to the preparation of *anti* and *syn* cryptophanes of large size (with spacer bridges at least up to $O(CH_2)_{10}O$). However, in contrast with the direct method, which furnishes *anti* cryptophanes with a high degree of stereoselectivity, we show that the template method affords mixtures of *anti* and *syn* stereomers, in a ratio depending on the even or odd number of methylenes in the spacer bridges. For the largest members of the family, we also demonstrate the existence of in–out topoisomers slowly equilibrating with the usual out–out forms.

Results and discussion

The template method is a convergent synthesis in which the building units **7** or **8** elaborated as depicted in figure 3 are linked to a suitable C_3-CTV triphenol such as cyclotriguaiacylene **11** leading to the cyclization precursors **13** shown in figure 4. These precursors are in turn converted into the corresponding mixture of cryptophanes **1** and **2** under acidic conditions.

For the preparation of triols **13**, the required intermediates **7** or **8** were obtained from vanillin **3** or vanillyl alcohol **4** by straightforward methods. Vanillin **3** in 95% ethanol was reacted with 1 equiv of 12 M NaOH then 1.8 equiv of a 1,ω-dibromoalkane to give **5c,f,h** and **i** in 50–60% yield, together with the corresponding dialkylated products **9** (0–10%). Likewise, vanillyl alcohol **4** was converted into **6d,e** and **g** in 60–69% yield by reaction with the corresponding dibromoalkanes in the presence of K_2CO_3 in acetone. This reaction also furnished 14–24% of the dialkylated products **10**. Conversion of the bromides **5** and **6** to the iodides **7** and **8**, respectively, was achieved (90–100%) by reaction with NaI in acetone.

The template unit C_3-cyclotriguaiacylene (±)-**11** was prepared by cyclodehydration of the *O*-allyl ether of vanillyl alcohol as described previously [20], and was resolved by chromatographic separation of its diastereomeric triesters with *R*-(+)-2-(4-chlorophenoxy)-propanoic acid. This resolution method actually proved to be easier than that reported earlier using ω-camphanic acid [21] as the resolving agent (details will be published separately). As the absolute configuration of cyclotriguaiacylene has been established to be *P*-(−), the reaction sequences depicted in figure 4 also fix the absolute configurations of the cryptophane precursors **12** and **13** (all *M*-(+)).

There is some flexibility in the preparation of precursors **13** from the above intermediates. Racemic **11** or its enantiomer *P*-(−)-**11** could be converted to (±)-**13** or *M*-(+)-**13**, respectively, in one step and ca 70% yield by reaction with the benzyl alcohol intermediates **8** in the presence of aqueous (6.25 M) NaOH in DMF/HMPA at room temperature. This procedure was followed for the preparation of **13d,e** and **g**. Alternatively, alkylation of the phenolic groups of (±)-**11** or (−)-**11** by the benzaldehyde intermediates **7** under the same conditions provided the trialdehydes (±)-**12** or *M*-(+)-**12** (ca 85%) which in turn were converted to **13** by reduction with $NaBH_4$ in methanol at room temperature (72–95%). This procedure was employed for the preparation of **13c,f,h** and **i**. In these syntheses, the choice of mild reaction conditions is dictated by the fact that optically active cyclotriveratrylenes racemize on heating, over a barrier of 110–115 kJ/mol, corresponding to

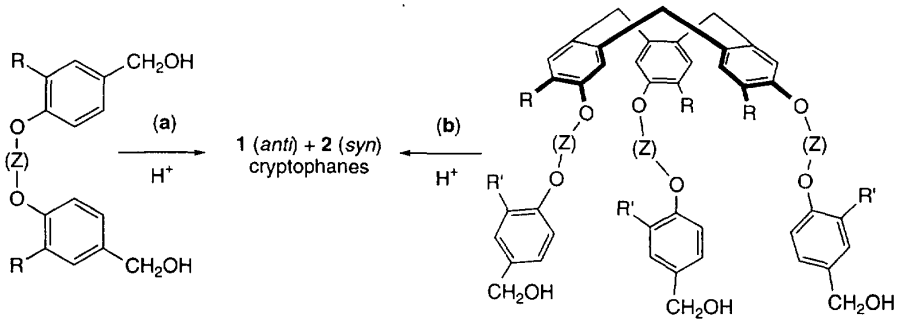
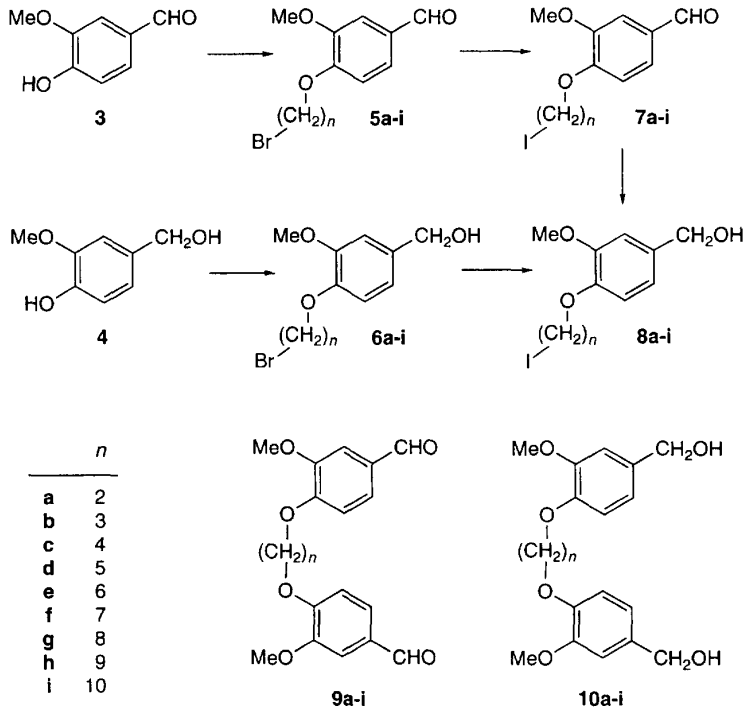


Fig 2. (a) Direct method and (b) template-directed cryptophane synthesis.



	n
a	2
b	3
c	4
d	5
e	6
f	7
g	8
h	9
i	10

Fig 3

the inversion of the cone conformation [1]. The inversion rate is negligible at room temperature but become quite significant above 60–70 °C.

For the conversion of the triol precursors **13** to the corresponding cryptophanes **1** and **2**, we employed conditions similar to those used in earlier works for the preparation of the smallest cryptophanes [4, 7, 10]. The racemic or resolved triol **13** was dissolved in a small volume of $CHCl_3$ (typically, 200 mg in 6 mL) and to this solution was added ca 450 mL of 99% formic acid, ensuring high dilution conditions (around 4×10^{-4} M). This solution was warmed at 55 °C for 3 h, or stirred for 15–24 h at room temperature (to avoid racemization) in reactions involving resolved **13**. Evaporation of the solvent under vacuum then afforded the desired cryptophane mixtures contaminated with relatively small amounts of more polar side products which were generally easily removed by chromatographic filtration over silica gel. The resulting cryptophane mixture was analyzed by ^1H NMR in order to determine the *anti/syn* ratio, and was then submitted to column or thin-layer chromatography in order to isolate the pure stereomers (whenever possible). All new cryptophanes (or mixtures thereof) gave FAB mass spectra in agreement with their elemental composition. In most cases the combustion analyses could only be interpreted by assuming the presence of guest species (water or organic solvents), which often were also visible in the NMR spectra. These spectra are relatively simple due to the symmetry of these molecules, and are characterized by the presence of the typical pattern of the CTV caps locked in crown conformation, consisting of an AX quartet for the H_a and H_e benzylic hydrogens of the methylene bridges (at ca 4.6 and 3.4 ppm, respectively, $J \approx 13.5$ Hz) and of two singlets for the aromatic hydrogens in the 6.7–6.8 ppm region. In general, the *anti* or *syn* stereochemistry, which cannot easily be deduced from the NMR spectra, was simply established on the basis of the optical activity