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SYNTHESIS OF NEW LIGANDS FOR TRANSITION METAL COMPLEXES: MENTHYL- AND NEOMENTHYL-CYCLOPENTADIENES

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Summary

Syntheses of (—)-menthylcyclopentadiene (MCp) and (+)-neomenthyl cyclopentadiene (NMCp) from (—)-menthol are described. These chiral ligands have been used to prepare $(\eta^5\text{-MCp})_2TiCl_2$, $(\eta^5\text{-NMCp})_2$,$TiCl_2$, $(\eta^5\text{-MCp})_2ZrCl_2$, $(\eta^5\text{-NMCp})_2ZrCl_2$, $(\eta^5\text{-Cp})(\eta^5\text{-MCp})TiCl_2$ and $(\eta^5\text{-Cp})(\eta^5\text{-NMCp})TiCl_2$. The structure and absolute configuration of $(\eta^5\text{-Cp})(\eta^5\text{-MCp})TiCl_2$ has been established by X-ray analysis.

Introduction

Asymmetric synthesis benefits greatly from the preparation of new chiral reagents or new chiral catalysts [1,2]. For example chiral boranes [3] enable one to obtain a large variety of chiral compounds of excellent optical purity. Chiral phosphines are now an essential component of many asymmetric rhodium catalysts [2,4,5]. More chiral ligands are needed for devising chiral systems specific for a given substrate.

One of the most common ligands in transition metal chemistry is the cyclopentadienyl group (Cp). It appears in several catalyst precursors such as $(\eta^5\text{-Cp})_2TiCl_2$ [6], $(Rh(\eta^5\text{-Cp})Cl_2)_2$ [7], $(\eta^5\text{-Cp})Cr(CO)_3)_2$ [8] and $(\eta^5\text{-Cp})Co(CO)_2$ [9]. The Cp ligand is also frequently encountered in complexes undergoing stochiometric reactions, such as $(\eta^5\text{-Cp})_2ZrClH$ [10] or $(\eta^5\text{-Cp})_2MoH_2$ [11]. It was thus interesting to prepare chiral cyclopentadienes * and we de-

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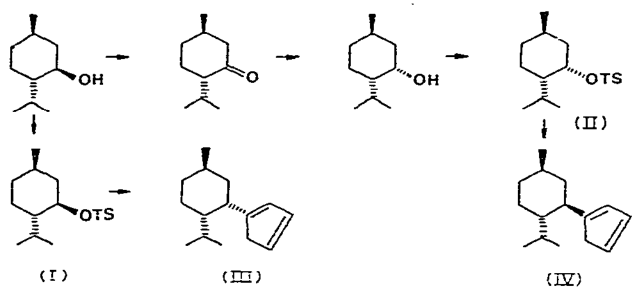
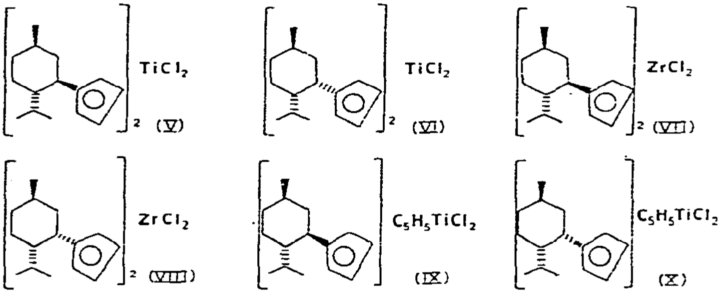
* The only monosubstituted chiral cyclopentadiene that we found mentioned in the literature was $CpCHCH_3Ph$ (17.3% optical purity) [12].

scribe below the synthesis of a new family of chiral cyclopentadiene ligands which can be attached to many transition metals.

Results and discussion

The (—)-menthol is taken as starting material for the synthesis, since it is an easily available chiral material. It is converted into (—)-menthyltosylate (I) or (—)-menthone. Reduction of (—)-menthone by Selectride affords (+)-neomenthol, which is then transformed into (+)-neomenthyltosylate II. Treatment of I or II with cyclopentadienylsodium salt leads to (+)-neomenthylcyclopentadiene (III) and (—)-menthylcyclopentadiene (IV), obtained as colourless high boiling oil, (see Scheme 1). GLC analysis and ^{1}H NMR spectra show each compound to be pure and free from the diastereoisomer. Both compounds are stable, even in solution, for up to three months without epimerisation. III and IV display a positive and negative Cotton effect, respectively (see the CD curves in Fig. 3c). We assume that the substitution on I and II occurred in each case with inversion of configuration. This hypothesis is supported by X-ray studies on IX.





It is known that 5-substituted cyclopentadienes are easily isomerized into 1- or 2-substituted cyclopentadienes ([13] and ref. therein). The NMR spectra of our compounds show only three vinylic signals, which means that the double bonds must be treated as in III, IV or one alternative structure. Careful examination of the NMR spectra in the 3 and 6 ppm areas is in agreement with a 1/1 mixture of 1- and 2-substituted cyclopentadienes. The result is confirmed by ^{13}C NMR, which ppm shows in the region δ 160—129 eight signals for MCp and

TABLE 1

PROPERTIES OF SUBSTITUTED CYCLOPENTADIENYL CHLORIDES OF TITANIUM(IV) AND ZIRCONIUM(IV)

Compound	Yield (%)	M.p. (°C ± 2)	Molecular formula	Analysis: (Found (calcd.) (%))		
				C	H	Cl
V	42.0	273	$C_{30}H_{46}TiCl_2$	67.8 (68.58)	8.58 (8.76)	14.2 (13.53)
VI	16.0	223	$C_{30}H_{46}TiCl_2$	68.36 (68.58)	8.77 (8.76)	14.35 (13.53)
VII	10.0	255	$C_{30}H_{46}ZrCl_2$	63.24 (63.36)	8.25 (8.10)	12.44 (12.50)
VIII	30.6	173	$C_{30}H_{46}ZrCl_2$	63.22 (63.36)	8.03 (8.10)	12.28 (12.50)
IX	35.0	204	$C_{20}H_{27}TiCl_2$	61.60 (62.03)	7.60 (7.24)	17.60 (18.35)
X	20.0	163	$C_{20}H_{27}TiCl_2$	60.62 (62.03)	7.20 (7.24)	17.90 (18.35)

a more complicated pattern (15 signals) for NMCP [*], suggesting in this latter case a mixture of more than two substituted cyclopentadienes. In our case each double bond position isomer will lead to the same cyclopentadienyl complex.

The lithium salts of III or IV are treated in benzene or THF with $TiCl_4$ or $ZrCl_4$ and the complexes V—VIII are isolated. The complexes IX and X are obtained by reaction between $CpTiCl_3$ and the lithium salt of III or IV respectively. Yields, physical and spectroscopic properties of the complexes V—X are listed in Tables 1 and 2.

The infrared spectra of all these complexes show the characteristic absorption of a Cp ring, centered about 3100 cm^{-1}. The four protons of the η^5-MCp and η^5-NMCp rings give separate signals in the 6—7 ppm region in the NMR spectra of V, VI and VIII. In VII two signals overlap. In the spectra of IX and X the five protons of η^5-C_5H_5 give one signal at 6.55 ppm, distinct from the four other signals due the chiral cyclopentadienyl ligand.

The titanium complexes V, VI, IX and X show reversible variations in the NMR spectra in the 6—10 ppm region between +20 and —40° C; no modifications are observed in the other regions of the spectra. The effect is particularly important in V and VI (Fig. 1,2). This must reflect conformational variations and we are currently studying the problem.

The zirconium complexes VII and VIII do not show any change in the 0—10 ppm region in the range —40 to + 100° C. The circular dichroism (CD) of V—X (Fig. 3a—3d) shows some similarities but much caution is needed in using it to assign absolute or relative configurations. The CD curves of the epimeric pairs, V and VI (Fig. 3b), VII and VIII (Fig. 3c) and IX and X (Fig. 3d) are quasi enantiomeric. If we consider homochiral pairs V, VII or VI, VIII the signs of the Cotton effects are similar only in the 330—400 nm region. The complexes with one chiral ligand and one Cp ligand show CD curves with different shapes

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[*] Throughout this paper menthylcyclopentadiene and neomenthylcyclopentadiene are abbreviated by MCp and NMCp, respectively.

TABLE 2

IR AND NMR DATA FOR SUBSTITUTED CYCLOPENTADIENYL CHLORIDES OF TITANIUM(IV) AND ZIRCONIUM(IV)

	IR [a, b] (cm^{-1})	NMR [e]
V	3100(m(s)), 3085, 1050(m(s)), 860(m(s)), 843(ss(s))	6.73 2H; 6.40 2H; 6.28 2H; 6.18 2H; 2.79 2H; 2.00—0.74 36H.
VI	3110(m(s)), 1050(m(s)), 855(ss(s)), 845(ss(s))	6.69 2H; 6.59 2H; 6.23 2H; 3.55 2H; 2.15—0.55 36 H.
VII	3100 [c] (m(s)), 1050(m(s)), 850(ss(s)), 835(ss(s))	6.57 2H; 6.33 2H; 6.10 4H; 2.36 2H; 1.91—0.71 36H.
VIII	3105(m(s), 1050(m(s)), 835 (ss(br))	6.63 2H; 6.44 2H; 6.17 2H; 6.13 2H; 3.41 2H; 2.17—0.55 36H.
IX	3120—3100 [d] (m(s), 1015(m(s)), 820(ss(s))	6.73 1H; 6.56 5H; 6.50 1H; 6.32 1H; 6.22 1H; 2.75 1H; 1.73—0.50 18H.
X	3120(m(br)), 1015(m(s)) 815(ss(br))	6.77 1H; 6.68 1H; 6.55 5H; 6.51 1H; 6.31 1H; 3.53 1H; 2.02—0.50 18H.

[a] All the IR spectra are recorded as KBr discs. [b] m = medium, ss = strong, (s) = sharp, (br) = broad. [c] The band presents a shoulder at lower energy. [d] Double band. [e] Chemical shifts (δ) in ppm (TMS internal standard), spectra at 250 MHz in $CDCl_3$.

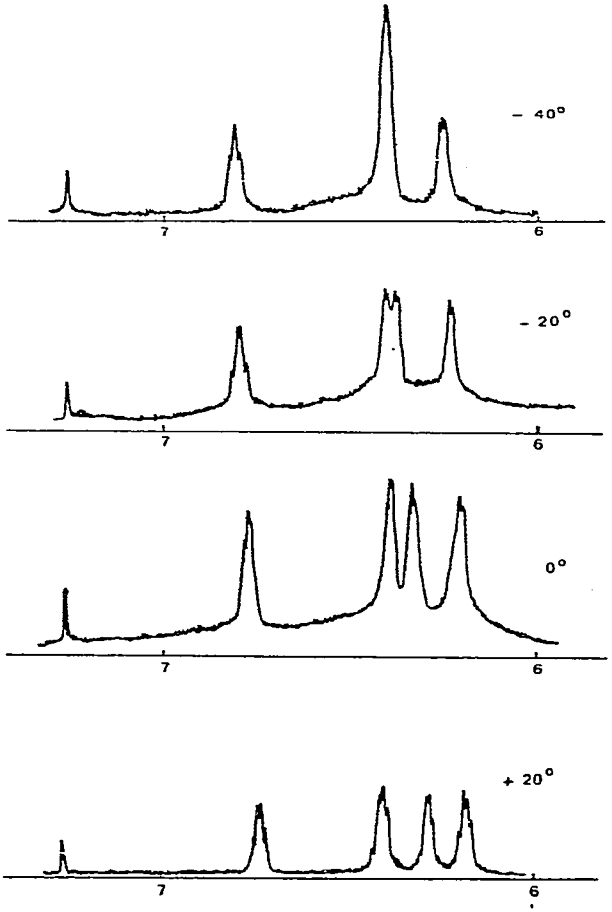

Fig. 1. Variable temperature ^1H NMR spectra of V in $CDCl_3$ (Cp ring protons region only).

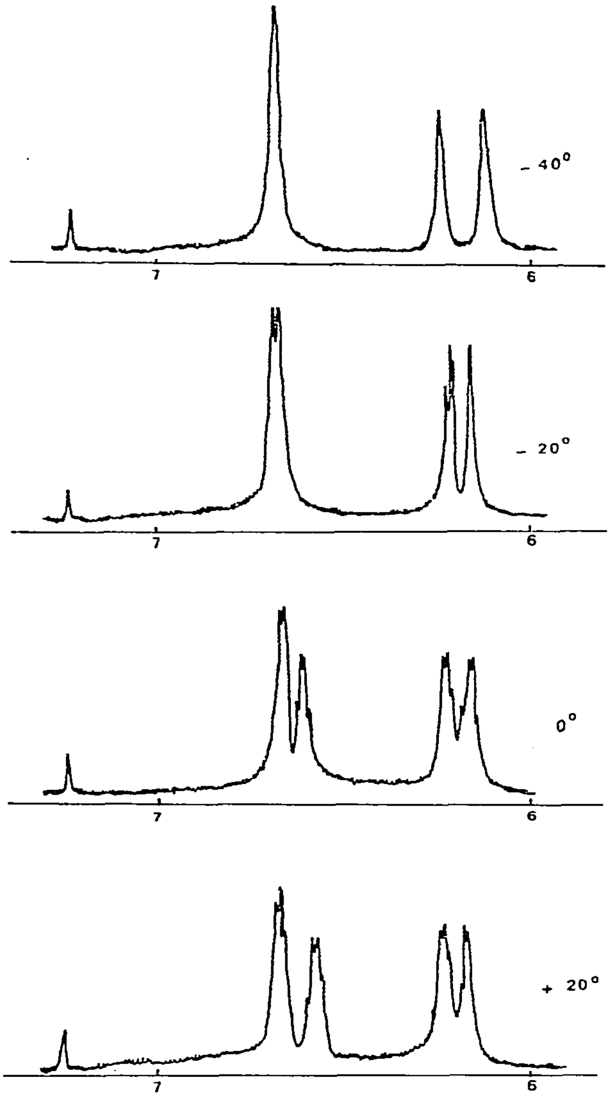

Fig. 2. Variable temperature ^{1}H NMR spectra of VI in $CDCl_3$ (Cp ring protons region only).

from those given by V—VIII, especially near and below 300 nm. It is difficult to deduce the configuration of the chiral ligands around the metal from the sign of the Cotton effect, nevertheless the 330 and 400 nm region is a good probe for stereochemical correlations when two identical chiral ligands are present in the complex. Because there are elements of comparison lacking it is difficult to discuss in more detail the multiple transitions which appear between 250 and 550 nm, most of them presumably involving the metal.

It is noteworthy that complexes $(\eta^5\text{-Cp})(\eta^5\text{-Cp}')Ti(C_6F_5)Cl$ and $(\eta^5\text{-Cp})(\eta^5\text{-Cp}')Ti(C_6F_5)OR$ with a chiral titanium atom were recently prepared and their chiroptical properties studied [14]. The CD curves of these compounds

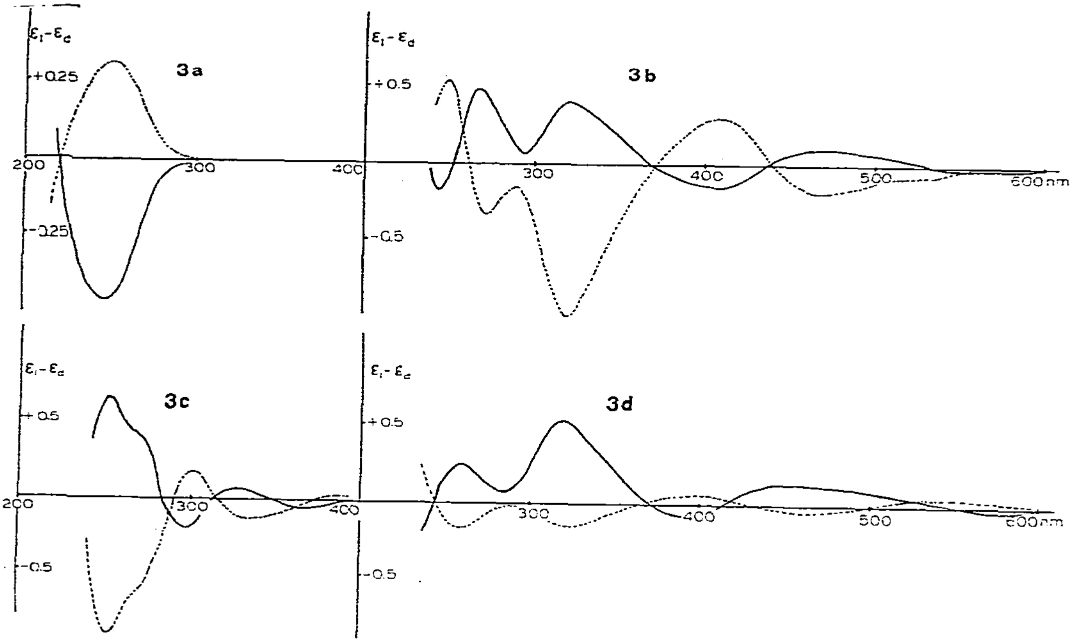

Fig. 3. CD spectra in $CHCl_3$ of: 3a: (· · · · · ·) III, (———) IV; 3b: (· · · · · ·) V, (———) VIc; 3c: (· · · · · ·) VIII, (———) VIII; 3d: (· · · · · ·) IX, (——— X.

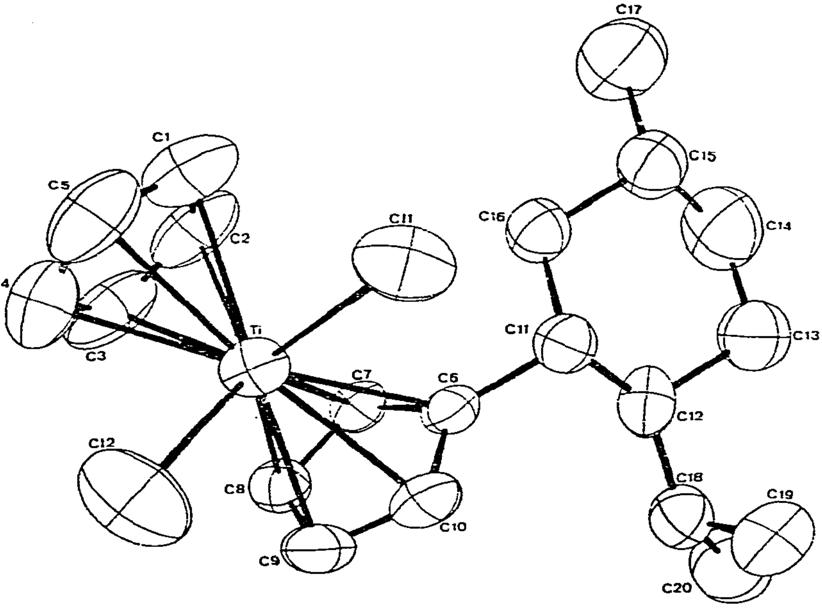

Fig. 4. The molecular structure of $(\eta^5\text{-Cp})(\eta^5\text{-MCp})TiCl_2$ (IX) showing the crystallographic numbering system.

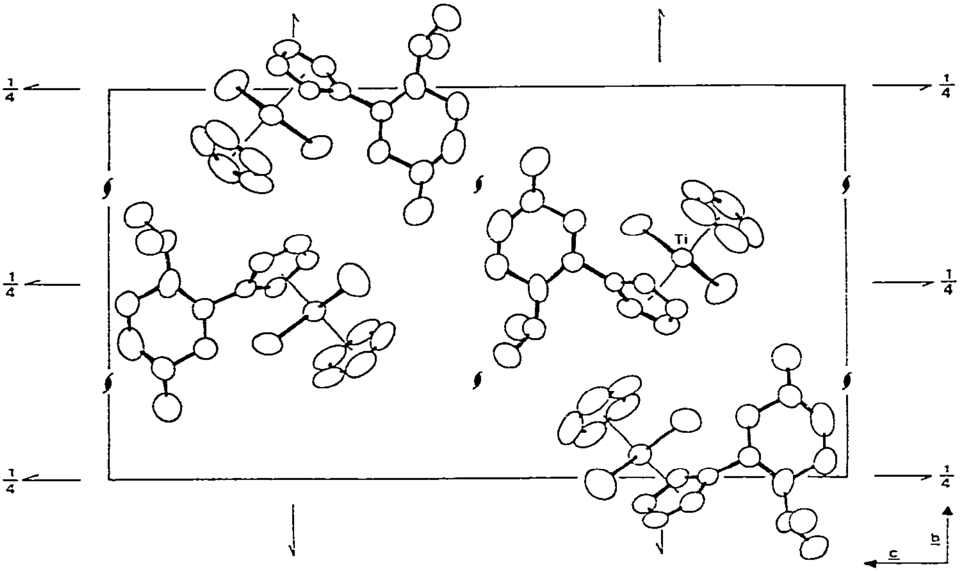

Fig. 5. The contents of the orthorhombic cell of IX seen in projection along a, looking towards the origin.

between 300 and 550 nm show the same kind of complexity as that encountered in the curves shown in Fig. 1b and 1d. They could be used in the 450 and 550 nm region for empirical stereochemical correlations.

Structure of IX by X-ray analysis

The red crystal chosen for intensity measurements was mounted on an Enraf—Nonius CAD-4 automatic diffractometer and intensities were collected as described previously [20]. The intensities were not corrected for the effects of absorption (μ 6.71 cm^{-1}). Pertinent crystal data are given in Table 4.

The structure was solved by conventional heavy atom methods and refined by blocked matrix least-squares with anisotropic thermal parameters ascribed to all non-hydrogen atoms. Hydrogen atoms were incorporated at calculated positions (C—H 0.95 Å) and their positions and thermal parameters were kept invariant during refinement (U_H 0.07 Å^2). Refinement converged at R 0.043, the mean shift to error ratio in the final cycle being 0.002. In the final electron density difference-synthesis peaks of 0.37 e Å^{-3} appeared in the neighbourhood of the metal atom, with much lower values elsewhere. Atomic scattering factors were those of Stewart, Davidson and Simpson [21] for hydrogen and Cromer and Waber for the remaining atoms [22]. In the case of Ti and Cl correction for the real and imaginary parts of anomalous dispersion was applied [23]. Refinement of the enantiomorphic structure resulted in an increase of the R factor to 0.045, R' 0.039. Application of the Hamilton significance test [24] establishes that the absolute configuration of the complex is the correct one at a 99.5% confidence level ($\mathcal{R}_{obs} = 1.106, \mathcal{R}_{1,2167,0.005} = 1.002$). The final positional and thermal parameters appear in Table 5; interatomic distances and angles are listed in Table 3. A listing of observed and calculated structure factors may be obtained upon request from one of the authors (C.K.).

(continued on p. 306)

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) [a]

(a) Distances

Ti—Cp(1)	2.064(3)	C(4)—C(5)	1.378(9)
Ti—Cp(2)	2.063(3)	C(5)—C(1)	1.354(9)
Ti—Cl(1)	2.367(1)	C(6)—C(7)	1.403(5)
Ti—Cl(2)	2.369(1)	C(6)—C(10)	1.419(6)
Ti—C(1)	2.393(5)	C(6)—C(11)	1.506(5)
Ti—C(2)	2.357(6)	C(7)—C(8)	1.409(6)
Ti—C(3)	2.362(7)	C(8)—C(9)	1.402(6)
Ti—C(4)	2.370(5)	C(9)—C(10)	1.393(6)
Ti—C(5)	2.368(7)	C(11)—C(12)	1.547(6)
Ti—C(6)	2.450(4)	C(11)—C(16)	1.534(6)
Ti—C(7)	2.379(4)	C(12)—C(13)	1.528(6)
Ti—C(8)	2.332(4)	C(12)—C(18)	1.544(7)
Ti—C(9)	2.374(4)	C(13)—C(14)	1.530(9)
Ti—C(10)	2.389(4)	C(14)—C(15)	1.512(8)
		C(18)—C(19)	1.510(9)
C(1)—C(2)	1.333(9)	C(18)—C(20)	1.501(8)
C(2)—C(3)	1.397(9)	C(15)—C(16)	1.513(7)
C(3)—C(4)	1.388(10)	C(15)—C(17)	1.506(8)

(b) Angles

Cl(1)—Ti—Cl(2)	94.8(1)	Cp(1)—Ti—Cl(2)	105.7(1)
Cp(1)—Ti—Cp(2)	132.9(1)	Cp(2)—Ti—Cl(1)	105.3(1)
Cp(1)—Ti—Cl(1)	105.7(1)	Cp(2)—Ti—Cl(2)	106.2(1)
C(10)—C(6)—C(11)	127.2(4)	C(7)—C(6)—C(11)	126.7(4)
C(6)—C(11)—C(16)	112.6(3)	C(6)—C(11)—C(12)	110.2(3)
C(11)—C(12)—C(13)	110.2(4)	C(12)—C(11)—C(16)	111.3(3)
C(13)—C(12)—C(18)	111.9(3)	C(11)—C(12)—C(18)	114.2(4)
C(12)—C(18)—C(20)	112.3(5)	C(12)—C(18)—C(19)	113.8(4)
C(12)—C(13)—C(14)	113.4(4)	C(19)—C(18)—C(20)	110.0(4)
C(14)—C(15)—C(16)	110.1(4)	C(13)—C(14)—C(15)	111.7(5)
C(16)—C(15)—C(17)	112.9(4)	C(14)—C(15)—C(17)	112.5(5)
		C(15)—C(16)—C(11)	112.9(4)

(c) Intermolecular distances less than 3.0 Å

Cl(1)—H(7)	2.77	C(12)—H(3)	2.78
Cl(2)—H(8)	2.96		

[a] Cp(1): C(1)—C(5) ring centroid, Cp(2): C(6)—C(10) ring centroid.

TABLE 4

CRYSTAL DATA

$C_{20}H_{28}TiCl_2$	*M* 387.3 amu
Crystal size: 0.15 × 0.08 × 0.09 mm	Crystal system: orthorhombic
$a = 6.501(1)$ Å	$V = 2055$ Å^3
$b = 13.335(3)$ Å	$Z = 4$
$c = 23.320(3)$ Å	$F(000) = 816$ e
space group: $P2_12_12_1$	$D_{calc} = 1.25$ g cm^{-3}
monochromatised Mo-K_α X-radiation:	$\lambda = 0.71069$ Å
$T = 17°$C	μ(Mo-K_α) = 6.71 cm^{-1}
scan type: $\theta - 2\theta$	max $2\theta = 56°$

3 monitor reflections measured every 100 reflections showed no significant variation during data-collection.

Total number of independent reflections measured: 4663 (± *h*, *k*, *l*)

Number of observed reflections $[I \geqslant 2.0\ \sigma(I)]$: 2375

Final $R = 0.043$

Final R' $(w = 1/\sigma^2(F_0)) = 0.036$

Goodness of fit $(\Sigma w(F_0 - F_c)^2)^{1/2}/(N - P) = 1.37$

TABLE 5

ATOMIC POSITIONAL PARAMETERS (FRACTIONAL COORDINATES × 10^4), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	*x*	*y*	*z*
Ti	2017(1)	5658(1)	2207(1)
Cl(1)	—269(1)	6487(1)	2833(1)
Cl(2)	—615(1)	4879(1)	1671(1)
C(1)	2815(11)	7344(3)	2003(2)
C(2)	4567(8)	6834(4)	1989(2)
C(3)	4514(10)	6165(4)	1534(3)
C(4)	2609(12)	6300(5)	1277(2)
C(5)	1564(8)	7014(4)	1580(3)
C(6)	3301(6)	5062(2)	3132(1)
C(7)	4889(5)	5036(2)	2725(1)
C(8)	4371(6)	4368(3)	2286(1)
C(9)	2450(7)	3960(2)	2422(2)
C(10)	1771(6)	4407(3)	2925(1)
C(11)	3337(6)	5580(3)	3703(1)
C(12)	4363(7)	4917(3)	4160(1)
C(13)	4489(9)	5460(3)	4733(1)
C(14)	5492(10)	6478(4)	4687(2)
C(15)	4429(8)	7116(3)	4246(2)
C(16)	4376(6)	6595(3)	3673(1)
C(17)	5341(12)	8135(4)	4210(2)
C(18)	3365(10)	3890(3)	4224(2)
C(19)	1177(10)	3919(3)	4440(2)
C(20)	4626(12)	3211(4)	4591(2)
H(1)	2472	7857	2267
H(2)	5685	6923	2248
H(3)	5568	5709	1428
H(4)	2058	5966	951
H(5)	213	7240	1502
H(7)	6127	5407	2745
H(8)	5160	4224	1955
H(9)	1767	3464	2214
H(10)	473	4296	3099
H(11)	1951	5704	3810
H(12)	5695	4778	4032
H(131)	5318	5076	4987
H(132)	3159	5532	4887
H(141)	6869	6405	4583
H(142)	5376	6791	5051
H(15)	3040	7230	4371
H(161)	3645	6991	3406
H(162)	5749	6507	3544
H(171)	5293	8461	4565
H(172)	6785	8074	4097
H(173)	4671	8514	3924
H(18)	3324	3632	3843
H(191)	1168	4218	4799
H(192)	385	4284	4172
H(193)	688	3262	4459
H(201)	5960	3124	4422
H(202)	4779	3475	4963
H(203)	3978	2579	4615

TABLE 5 (continued)

ANISOTROPIC THERMAL PARAMETERS ($\times 10^3$)[a]

Atom	$U_{1,1}$	$U_{2,2}$	$U_{3,3}$	$U_{1,2}$	$U_{1,3}$	$U_{2,3}$
Ti	36	48	59	−1	−6	5
Cl(1)	47	63	94	9	−2	−11
Cl(2)	53	117	108	−6	−25	−33
C(1)	99	60	119	−8	−4	28
C(2)	61	91	120	−23	−5	56
C(3)	97	86	125	34	65	56
C(4)	134	120	57	−19	−11	30
C(5)	73	106	106	28	−18	47
C(6)	50	41	48	1	1	9
C(7)	38	48	49	5	−2	10
C(8)	68	46	56	12	4	1
C(9)	91	37	70	−11	−15	3
C(10)	65	47	66	−15	8	11
C(11)	51	52	51	−3	4	0
C(12)	73	78	48	13	6	7
C(13)	120	90	54	0	−15	6
C(14)	142	126	66	−29	−14	−19
C(15)	116	77	60	−29	4	−9
C(16)	73	68	56	−13	−4	−2
C(17)	231	102	79	−65	−10	−15
C(18)	131	57	49	14	8	12
C(19)	143	82	81	−27	25	14
C(20)	224	90	72	48	21	15

[a] Anisotropic thermal parameters in the form $\exp\{-2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]\}$

The molecular structure of IX is given in Fig. 4, together with the crystallographic numbering scheme, while the contents of the orthorhombic unit cell is shown in Fig. 5. The two chlorine atoms and the centroids of the two cyclopentadienyl rings formally occupy four tetrahedral-like coordination sites about the central metal atom; the most significant deviation from the tetrahedral form is at Cl(1)—Ti—Cl(2) and Cp(1)—Ti—Cp(2), where the respective angles at Ti are 94.8° and 132.9°. The geometry of the Cp_2TiCl_2 moiety is similar to that found in $[(\eta\text{-}C_5H_5)_2TiCl_2]$ [25], $[\eta\text{-}C_5H_4CH_3)_2TiCl_2]$ [26], $[(\eta\text{-}C_5H_5)[(CH_3)_5C_5]\text{-}TiCl_2]$ [27] and $[(\eta\text{-}C_5(CH_3)_5)_2TiCl_2]$ [28] except that the cyclopentadienyl rings adopt an eclipsed conformation. These rings are approximately planar (mean out of plane distance in each ring = 0.01 Å) in spite of the fact that C(6), the link to the chiral group, is significantly further from Ti than the other cyclopentadienyl ring carbon atoms. The planes of the two rings make an angle of 131° to one another. The stereochemistry of the chiral group shows the menthyl structure is retained, and the chiral carbon atoms have the configurations C(12) *S*, C(15) *R* and C(11) *R*. Of particular interest is the configuration of C(11), which demonstrates that the substitution at neomenthyltosylate by sodium cyclopentadienide is accompanied by inversion of configuration (giving (—)-IV). It can be inferred that (+)-III obtained from menthytosylate has a neomenthyl stereochemistry.

We are currently investigating the use of titanium complexes V, VI, IX and X as precursors of chiral catalysts and the zirconium complexes VII and VIII as precursors of chiral reagents.

Experimental

A. Apparatus and techniques

Microanalyses for C, H and Cl were performed by the Service Central de Microanalyse du CNRS. Melting points were determined with a Kofler—RCH melting apparatus and are uncorrected. The IR spectra were obtained on a Perkin—Elmer Model 257 grating spectrophotometer. ^{1}H NMR spectra were recorded on a Cameca 250 MHz spectrophotometer, chemical shifts are reported in ppm relative to tetramethylsilane (δ). GLC were performed on a Carlo—Erba Fractovap GI using the following columns: Carbowax 20M to check the purity of (—)-menthol, (—)-menthone, (+)-neomenthol; OV-A to check the purity of (—)-menthylcyclopentadiene and (+)-neomenthylcyclopentadiene.

Optical rotations were measured on a Perkin—Elmer polarimeter 141. CD were recorded on a Jobin—Yvon D-2A apparatus. X-ray analysis of IX was performed at the Max-Planck Institut für Kohlenforschung in Mülheim, Germany.

All the reactions were carried out under N_2. Solvents were purified by distillation from $LiAlH_4$ (THF) or from $Na(C_6H_6)$ and stored under N_2.

B. Synthesis

Oxidation of (—)-menthol to (—)-menthone. 53.5 g CrO_3 in 46 ml H_2SO_4 and 200 ml H_2O are slowly added to a solution of 83.5 g (—)-menthol ($[\alpha]_D^{25}$ —46.0°, *c* 10, EtOH) in 100 ml acetone at 0°C. After separation and distillation 58.5 g (—)-menthone are recovered: $[\alpha]_D^{25}$ —25.3° (lit. $[\alpha]_D^{25}$ —28°) [15]. GLC analysis shows the (—)-menthone to be 96% pure with 3% of isomenthone and traces of unreacted (—)-menthol.

Reduction of (—)-menthone to (+)-neomenthol. (—)-Menthone is reduced to (+)-neomenthol in accordance to the modified method reported in ref. 16. (+)-Neomenthol: $[\alpha]_D^{22}$ + 17.8° (lit. [17] $[\alpha]_D^{22}$ + 19.6°). GLC shows that the (+)-neomenthol is 95% pure, contaminated with 5% of (—)-menthol.

Tosylate of (—)-menthol and (+)-neomenthol. Neomenthyltosylate II and menthyltosylate III are prepared as described in ref. 18 and ref. therein.

Preparation of (—)-menthylcyclopentadiene (IV). Sodium cyclopentadienide is prepared according to ref. 19. 63.5 ml (0.77 mol) of freshly distilled C_5H_6 is added to 17.7 g of sodium sand suspended in 400 ml THF under N_2. The solution of sodium cyclopentadienide is added slowly, the solution of (+)-neomenthyltosylate in 100 ml THF, the temperature being kept between 0 and 5°C. After the addition is finished, the solution is warmed slowly, and then refluxed for 1 h. The solution is then cooled, treated with 50 ml H_2O and the volatile organic products and the solvent are removed in vacuo. The aqueous solution is extracted with ether (5 × 50 ml), dried over sodium sulfate, evaporated from the solvent and then distilled in vacuo. The fraction 70—80°C/0.5 mmHg gives 12.5 g of a colourless oil; yield, based on (+)-neomenthol is 31.5%. $[\alpha]_D^{20}$ —51.8° ± 0.5 (*c* 3.56, $CHCl_3$). ^{1}H NMR (in $CHCl_3$): 0.6—2.6 (18H), 2.74 (1H), 2.86 (2H), 5.8—6.5 (3H). Anal.: Found: C, 87.55; H, 11.86. $C_{15}H_{24}$ calcd.: C, 88.23; H, 11.76%. GLC analysis shows the compound pure and free from neomenthylcyclopentadiene.

Preparation of (+)-neomenthylcyclopentadiene (III). 100 g of (—)-menthyltosylate are treated in a similar manner as described for the preparation of

(—)-menthylcyclopentadiene (IV). The fraction collected between 75 and 85°C/1 mmHg gives 16 g of (+)-neomenthylcyclopentadiene as a colourless oil. The yield is 24.3% based on (—)-menthyltosylate. $[\alpha]_D^{25}$ + 33.0 ± 0.5 (*c* 3.10, $CHCl_3$). ^1H NMR (in $CHCl_3$): 0.7—2 (18H), 2.9 (2H), 3 (1H), 6.05—6.55 (3H). Anal.: Found: C, 87.45; H, 11.90. $C_{15}H_{24}$ calcd.: C, 88.23; H, 11.76%. GLC analysis shows the compound to be pure and free from (—)-menthylcyclopentadiene.

Preparation of substituted cyclopentadienyl compounds of titanium(IV) and zirconium(IV). The procedure for the preparation of the bis-cyclopentadienyl complexes is very similar in all cases but the work-up and isolation is different in each case. Standard procedure: 1.5 g (7.35 mmol) of III or IV are dissolved in 15 ml THF under nitrogen and 1 equiv. of methyllithium (2.05 *M* in ether) is added dropwise. The solution is stirred for 1 h and cooled to 0° C. The solution is then added dropwise to a cold solution of 683 mg (3.60 mmol) of $TiCl_4$ in 15 ml benzene to give V or VI, or into a cold suspension of 856 mg (3.60 mmol) in 15 ml THF to give VII or VIII. Yields and physical data are listed in Table 1. IR and NMR data in Table 2.

Bis(menthylcyclopentadienyl)titanium(IV) chloride ($(MCp)_2TiCl_2$, V). After the addition of the solution of the lithium salt of IV is complete, the brown heterogeneous solution is stirred overnight at room temperature. The solvent is removed under vacuo while the residue turns deep green. Washing with water and ether leaves a red-brown solid which is dissolved in boiling chloroform. The chloroform solution, reduced to small volume, is set aside overnight at 0° C to give 800 mg of V as bright red crystals.

Bis(neomenthylcyclopentadienyl)titanium(IV) chloride ($(NMCP)_2TiCl_2$ (VI). The deep red solution (after addition of the lithium salt solution of III) is stirred overnight, then filtered from the white solid (LiCl). The solution is treated with a few drops of water to eliminate the unreacted $TiCl_4$ and evaporated at reduced pressure. The red brown solid is dissolved in ether. This solution is dried over $CaCl_2$, filtered, and reduced to small volume; after standing overnight at 0° C it gives 307 mg of VI as deep red, well formed crystals.

Bis(menthylcyclopentadienyl)zirconium(IV) chloride ($(MCp)_2TiCl_2$, VII. The pale yellow suspension resulting from the addition of the lithium salt solution of IV, is stirred overnight. A few drops of water are added and the solution is evaporated at reduced pressure. The yellow brown solid is repeatedly extracted with boiling chloroform in a Soxhlet apparatus. The chloroform solution is evaporated, and the brown solid recrystallized from MeOH to yield 200 mg of white, well formed crystals of VII.

Bis(neomenthylcyclopentadienyl(zirconium(IV) chloride ($(NMCp)_2ZrCl_2$, VIII). The yellow suspension resulting from the addition of the lithium salt of III is filtered and evaporated under reduced pressure. The brown solid is dissolved in chloroform and the solution washed with water. The organic layer is separated and dried over $CaCl_2$, and the solvent removed in vacuo. The solid is recrystallized from MeOH/$CHCl_3$ 4/1 to yield 870 mg of VIII as white chrystals.

Cyclopentadienylmenthylcyclopentadienyltitanium(IV) chloride (IX) and cyclopentadienylneomenthylcyclopentadienyltitanium(IV) chloride (X). To a solution of 0.5 g of $CpTiCl_3$ in 10 ml of THF under nitrogen at 0° C is slowly added 10 ml of a cold solution of the lithium salt of III or IV (1 eq.). The temperature is allowed to rise to 25° C. After 1 h of stirring at room temperature the deep red solution is evaporated, and the solid repeatedly extracted with boiling hexane in a Soxhlet apparatus. After cooling the hexane solution and standing at 0° C overnight, bright red crystals of IX or X are obtained.

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