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XI *. Synthesis of some new chiral cyclopentadienyl-titanium and -zirconium complexes and crystal structures of $[R\text{-}CH_3OCH_2CH(CH_3)Cp]_2MCl_2$ (M = Ti, Zr)

Qichen Huang and Yanlong Qian **

Shanghai Institute of Organic Chemistry, Academia Sinica, Shanghai (China)

and Youqi Tang

Institute of Physical Chemistry, Peking University, Beijing (China)

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Abstract

Twelve new chiral cyclopentadienyl-titanium or -zirconium complexes Cp'_2TiCl_2, $Cp'CpTiCl_2$ and Cp'_2ZrCl_2, (Cp = η^5-cyclopentadienyl and Cp′ = $CH_3OCH(R')CH(R'')Cp$), have been synthesized. Complex (*R*,*R*)-**1** and (*R*,*R*)-**3** have been studied by X-ray analysis. The complex (*R*,*R*)-**1** forms violet-red plate crystals, which are triclinic, space group *P*1, with *a* 6.775(3), *b* 6.792(4), *c* 35.517(22) Å, *α* 89.94(5), *β* 90.05(4), *γ* 119.98(4)°, *V* 1415(1) Å^3, *Z* = 3. The structure was refined to an *R* factor of 0.039 for 3142 observed reflections. The complex (*R*,*R*)-**3** forms colorless plate crystals, and is isomorphous with (*R*,*R*)-**1**, *a* 6.8295(6), *b* 6.8301(6), *c* 35.940(2) Å, *α* 89.990(7), *β* 90.011(7), *γ* 119.997(6)°, *V* 1541.9(2) Å^3. The final *R* factor is 0.065 for 2608 observed reflections.

Introduction

Asymmetric synthesis benefits greatly from the preparation of new chiral reagents or new chiral catalysts. Cyclopentadienyl (Cp) is a very common type of ligand in organometallic chemistry. It is found in many catalyst precursors such as Cp_2TiCl_2, Cp_2V and Cp_2Ni. The Cp ligand is also frequently encountered in complexes undergoing stoichiometric reaction, such as Cp_2ZrClH or Cp_2MoH_2. The synthesis of new chiral cyclopentadienes and their complexes is therefore of

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** Author to whom correspondence should be addressed.

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interest. However, the synthesis of chiral cyclopentadienes is still limited to a few examples, such as $CpCH(CH_3)Ph$ [1], menthylcyclopentadienyl [2], neomenthylcyclopentadienyl [2] and other chiral cyclopentadienyl [3–10] ligands. These ligands have in common large chiral substituents on a cyclopentadienyl ring. We describe below the synthesis and crystal structure of a new family of chiral cyclopentadienyltitanium complexes, which have chiral side chains containing an ethereal oxygen atom.

Experimental

All experiments were carried out under argon with standard techniques.Solvents were distilled under argon from sodium before use. ^1H NMR spectra were obtained using a EM-360 NMR Spectrometer. ^{13}C NMR spectra were recorded on a Varian XL-200 Spectrometer. IR srectra were obtained using a Shimadzu IR-440 Spectrometer. The MS spectrum was measured on a Finnigan 4021 Mass Spectrometer. Specific rotation was measured on a Perkin–Elmer 241 MC Polarimeter. Melting points were not corrected.

All titanium complexes are red, while the zirconium complexes are colorless. The typical procedure, using (*R*,*R*)-**1** as an example, is described below:

A solution of 18.9 g (0.137 mol) of *R*-$CH_3OCH_2CH(CH_3)CpH$ in 100 ml THF was added to a suspension of 5.36 g of potassium sand and 100 ml of THF with stirring under argon. Stirring was continued for 2 h. After 0.7 g of unreacted potassium was removed, 202 ml of an approximately 0.589 *M* THF solution of Cp'K was obtained.

A solution of 1.92 ml (3.32 g) of $TiCl_4$ in 18 ml dry benzene was added in a Schlenk flask. Then 60 ml of the Cp'K solution was added at 0 °C, and the mixture was stirred for an additional 2 h. The solvent was removed under vacuum, and the solid residue was extracted with ether. The extracts were concentrated, cooled to −78 °C, and filtered to give a red solid product, (*R*,*R*)-**1**, 4.2 g, yield 61%.

The complexes prepared are listed in Table 1. The zirconium complexes were prepared similarly.

Crystal data and experiment parameters

The crystals of both complexes (*R*,*R*)-**1** and (*R*,*R*)-**3** were obtained by recrystallization from benzene under an argon atmosphere. The diffraction intensities of crystal (*R*,*R*)-**1** were measured on a Syntex P3/R3 four-circle diffractometer, using Mo-K_α radiation with a graphite monochromator, λ 0.71069 Å. The crystal of (*R*,*R*)-**3** was measured on a Rigaku AFC-5R diffractometer using a Cu-K_α (Ni filter), 1.54178 Å. The crystal data and other experimental parameters are listed in Table 2. Both crystals are isomorphous, and their crystal dimensions suggest that they belong to a trigonal or hexagonal system. However their diffraction intensities did not have symmetry higher than triclinic.

The intensities were corrected for Lorentz and polarization effects but not for absorption effects.

Structure solution, refinement and absolute configuration

For (*R*,*R*)-**1**, three titanium atoms and six chlorine atoms were found by the direct method using the SHLEXTL 3.0 program system, and the remaining non-hydrogen atoms were found on a Fourier map. After refinement with anisotropic

Table 1

Chiral cyclopentadienyl complexes prepared

Product	Yield (%)	m.p. (°C)	Elemental analysis (Found (calcd.) (%))			^{1}H NMR (TMS, $CDCl_3$) δ (ppm)	^{13}C NMR ($CDCl_3$, δ 77.10) δ (ppm)	MS (m/z)	IR (KCl) ν_{max} (cm^{-1})	$[\alpha]_D$ (c, t °C) (in benzene)
			C	H	Ti					
(*R*,*R*)-**1**	61	136–137	55.45	6.97	12.21	1.24d, 1.58m,	141.53, 121.28, 119.91,	357(M^+ – Cl),	3150m, 860s,	+173° (0.10, 24)
(*S*,*S*)-**1**			(54.98	6.66	12.18)	3.35s, 3.45d,	116.59, 114.89, 77.69,	255, 219	880m, 1080m,	
						6.40d	58.81, 34.89, 16.54		1100ss	
(*R*)-**2**	98	134–135	52.79	6.05	15.26	1.24d, 1.58m,	142.06, 121.52, 120.30,	285(M^+ – Cl),	3100s, 840ss,	+53°(0.10, 22.5)
(*S*)-**2**			(52.37	5.65	14.92)	3.35s, 3.45d,	117.27, 115.62, 119.77	255, 219,	860m, 1050m,	
						6.44d, 6.54s	77.64, 58.81, 34.89,	183, 148	1090ss	
							16.59			
(*R*,*R*)-**3**	65	104–105	50.03	6.33		1.24d, 1.58m,	137.43, 116.20, 115.28,	434(M^+),	3100m, 840ss,	+32°(0.90, 25)
(*S*,*S*)-**3**			(49.53	6.00)		3.35s, 3.45d,	113.27, 110.98, 78.16,	399(M^+ – Cl),	860s, 1048s	
						6.30d	58.76, 34.26, 16.83	297, 261	1090ss	
(*S*,*S*)-**4**	55	127–128	54.63	6.73	12.44	1.10d, 2.78d,	134.01, 124.26, 115.62,	357(M^+ – Cl),	3100m, 810s,	
(*R*,*R*)-**4**			(54.98	6.66	12.18)	3.30s, 3.48m,	114.69, 76.62, 56.12,	255, 219	855s, 1060m,	
						6.37d	37.53, 19.27		1100s	
(*S*)-**5**	52	88–90	52.69	5.90	15.03	1.10d, 2.78d,	134.75, 124.99, 124.30,	285(M^+ – Cl),	3100s, 840s,	
(*R*)-**5**			(52.37	5.65	14.92)	3.30s, 3.48m,	115.96, 114.93, 119.71,	255, 219,	865m, 1050m,	
						6.39d, 6.50s	76.62, 56.17, 37.58,	183, 148	1100s	
							19.27			
(*S*,*S*)-**6**	10	84–86	49.20	6.04		1.10d, 2.78d,	130.65, 118.59, 118.30,	399(M^+ – Cl),	3100m, 840m,	
(*R*,*R*)-**6**			(49.53	6.00)		3.30s, 3.48m,	112.69, 112.10, 77.25,	297, 261	860m, 1045s,	
						6.28d	56.32, 36.94, 19.27		1100s	

Table 2

Crystal data

Compound	(*R*,*R*)-**1**	(*R*,*R*)-**3**
Formula weight	$C_{18}H_{26}O_2Cl_2Ti/393.2$	$C_{18}H_{26}O_2Cl_2Zr/436.5$
Colour and habit	red/plates	colourless/plates
Crystal system	triclinic	triclinic
Space group	*P*1	*P*1
a (Å)	6.775(3)	6.8295(6)
b (Å)	6.792(4)	6.8301(6)
c (Å)	35.52(2)	35.940(2)
α (°)	89.94(5)	89.990(7)
β (°)	90.05(4)	90.011(7)
γ (°)	119.98(4)	119.997(6)
V (Å^3)	1415(1)	1541.9(2)
Z	3	3
Dc (g cm^{-3})	1.38	1.50
μ (cm^{-1})	7.6 (Mo-K_α)	75.3 (Cu-K_α)
F (000)	618	672
Scan method	$\theta-2\theta$	$\omega-2\theta$
Max. 2θ (°)	45	100
Crystal size (mm)	$0.06\times0.5\times0.5$	$0.15\times0.3\times0.35$
Scan rate (° min^{-1})	6–30	128
No. of observed reflections	3142 $I>1.96\sigma(I)$	2608 $I>3.0\sigma(I)$
R	0.039	0.065
R_w	0.037 $w=1/\sigma^2(F)+0.00025F)$	0.063 $w=1/(\sigma^2(F)+0.00025F)$
GOF	1.772	2.682

temperature factors by full-matrix-block least-squares, a difference map was calculated, most hydrogen atoms were located, and the others were placed at calculated positions (C–H 0.96 Å). Further refinement converged at $R = 0.039$.

The structure of complex (*R*,*R*)-**3** was directly refined using the coordination of (*R*,*R*)-**1**, only with zirconium atoms instead of titanium atoms. Its absolute config-

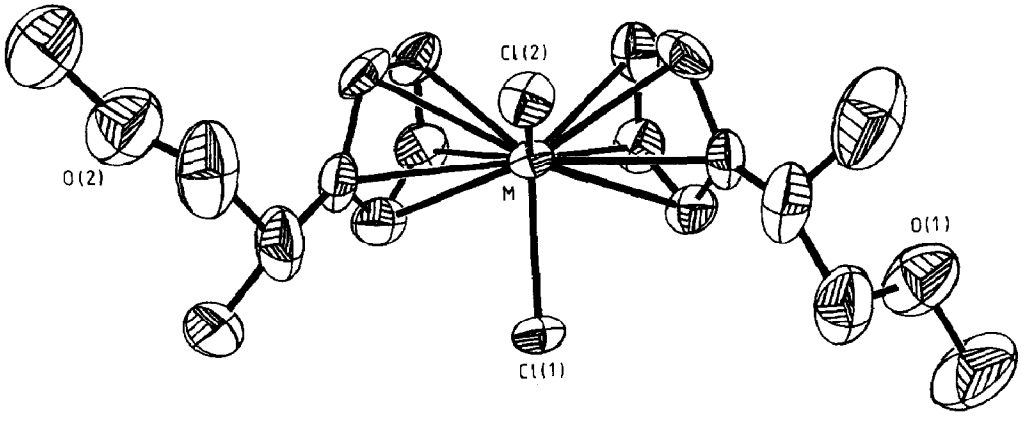

Fig. 1

Table 3

Selected bond lengths and angles for crystal (*R*,*R*)-**1**

Bond lengths (Å)					
Ti(1)–Cl(1)	2.378(2)	Ti(2)–Cl(3)	2.366(2)	Ti(3)–Cl(5)	2.372(2)
Ti(1)–Cl(2)	2.375(1)	Ti(2)–Cl(4)	2.379(2)	Ti(3)–Cl(6)	2.373(3)
Ti(1)–C(101)	2.464(8)	Ti(2)–C(201)	2.450(8)	Ti(3)–C(301)	2.435(8)
Ti(1)–C(102)	2.407(9)	Ti(2)–C(202)	2.410(8)	Ti(3)–C(302)	2.408(7)
Ti(1)–C(103)	2.348(8)	Ti(2)–C(203)	2.344(8)	Ti(3)–C(303)	2.342(8)
Ti(1)–C(104)	2.339(12)	Ti(2)–C(204)	2.354(7)	Ti(3)–C(304)	2.339(10)
Ti(1)–C(105)	2.387(10)	Ti(2)–C(205)	2.389(9)	Ti(3)–C(305)	2.395(9)
C(101)–C(102)	1.379(10)	C(201)–C(202)	1.406(13)	C(301)–C(302)	1.408(9)
C(102)–C(103)	1.384(15)	C(202)–C(203)	1.399(10)	C(302)–C(303)	1.400(14)
C(103)–C(104)	1.395(12)	C(203)–C(204)	1.403(15)	C(303)–C(304)	1.387(13)
C(104)–C(105)	1.382(14)	C(204)–C(205)	1.383(10)	C(304)–C(305)	1.394(11)
C(105)–C(101)	1.432(15)	C(205)–C(201)	1.432(12)	C(305)–C(301)	1.427(15)
C(101)–C(106)	1.501(15)	C(201)–C(206)	1.509(10)	C(301)–C(306)	1.517(15)
C(106)–C(107)	1.532(15)	C(206)–C(207)	1.541(19)	C(306)–C(307)	1.486(15)
C(106)–C(108)	1.525(19)	C(206)–C(208)	1.493(18)	C(306)–C(308)	1.476(19)
C(108)–O(1)	1.354(15)	C(208)–O(3)	1.379(14)	C(308)–O(5)	1.389(14)
O(1)–C(109)	1.448(14)	O(3)–C(209)	1.440(21)	O(5)–C(309)	1.430(16)
Ti(1)–C(111)	2.459(8)	Ti(2)–C(211)	2.451(8)	Ti(3)–C(311)	2.444(8)
Ti(1)–C(112)	2.413(8)	Ti(2)–C(212)	2.414(9)	Ti(3)–C(312)	2.396(7)
Ti(1)–C(113)	2.351(10)	Ti(2)–C(213)	2.351(8)′	Ti(3)–C(313)	2.327(8)
Ti(1)–C(114)	2.362(8)	Ti(2)–C(214)	2.348(7)	Ti(3)–C(314)	2.351(10)
Ti(1)–C(115)	2.416(8)	Ti(2)–C(215)	2.412(9)	Ti(3)–C(315)	2.398(9)
C(111)–C(112)	1.425(13)	C(211)–C(212)	1.392(13)	C(311)–C(312)	1.411(9)
C(112)–C(113)	1.392(12)	C(212)–C(213)	1.413(10)	C(312)–C(313)	1.405(15)
C(113)–C(114)	1.398(10)	C(213)–C(214)	1.404(15)	(313)–C(314)	1.381(12)
C(114)–C(115)	1.399(15	C(214)–C(215)	1.382(10)	C(314)–C(315)	1.405(12)
C(115)–C(111)	1.408(9)	C(215)–C(211)	1.429(13)	C(315)–C(311)	1.423(15)
C(111)–C(116)	1.507(15)	C(211)–C(216)	1.519(11)	C(11)–C(316)	1.525(15)
C(116)–C(117)	1.503(15)	C(216)–C(217)	1.491(19)	C(316)–C(317)	1.497(17)
C(116)–C(118)	1.526(14)	C(216)–C(218)	1.500(18)	C(316)–C(318)	1.481(14)
C(118)–O(2)	1.371(16)	C(218)–O(4)	1.379(12)	C(318)–O(6)	1.408(15)
O(2)–C(119)	1.447(13)	O(4)–C(219)	1.447(19)	O(6)–C(319)	1.436(13)
Ti(1)–Cp(1) [a]	2.074	Ti(2)–Cp(3)	2.064	Ti(3)–Cp(5)	2.058
Ti(1)–Cp(2)	2.078	Ti(2)–Cp(4)	2.069	Ti(3)–Cp(6)	2.059
Bond angles (°)					
Cl(1)–Ti(1)–Cl(2)	92.9(1)	Cp(1)–Ti(1)–Cp(2)	133.2		
C(101)–C(106)–C)107)	111.0(1)	C(101)–C(106)–C(108)	112.7(7)		
C(107)–C(106)–C(108)	111.8(9)	C(106)–C)108)–O(1)	109.1(13)		
C(108)–O(1)–C(109)	109.0(11)	C(111)–C(116)–C(117)	112.4(8)		
C(111)–C(116)–C(118)	111.9(10)	C(117)–C(116)–C(118)	112.9(9)		
C(116)–C(118)–O(2)	109.4(8)	C(118)–O(2)–C(119)	112.8(8)		
Cl(3)–Ti(20–Cl(4)	92.7(1)	Cp(3)–Ti(2)–Cp(4)	133.1		
C(201)–C(206)–C(207)	111.0(8)	C(201)–C(206)–C(208)	114.0(9)		
C(207)–C(206)–C(208)	112.8(9)	C(206)–C(208)–O(3)	109.0(9)		
C(208)–O(3)–C(209)	111.2(10)	C(211)–C(216)–C(217)	111.9(9)		
C(211)–C(216)–C(218)	111.6(9)	C(217)–C(216)–C(218)	113.5(9)		
C(216)–C(218)–O(4)	109.6(9)	C(218)–O(4)–C(219)	112.3(9)		
Cl(5)–Ti(3)–Cl(6)	92.6(1)	Cp(5)–Ti(3)–Cp(6)	132.8		
C(301)–C(306)–C(307)	114.0(12)	C(301)–C(306)–C(308)	112.1(7)		
C(307)–C(306)–C(308)	113.5(9)	C(306)–C(308)–O(5)	109.8(12)		
C(308)–O(5)–C(309)	112.8(11)	C(311)–C(316)–C(317)	111.9(8)		
C(311)–C(316)–C(318)	113.3(11)	C(317)–C(316)–C(318)	113.6(9)		
C(316)–C(318)–O(6)	109.0(7)	C(318)–O(6)–C(319)	111.3(8)		

[a] Cp is the centre of the cyclopentadienyl ring.

Table 4

Selected bond lengths and angles for crystal (*R*,*R*)-3

Bond lengths (Å)					
Zr(1)–Cl(1)	2.448(7)	Zr(2)–Cl(3)	2.440(7)	Zr(3)–Cl(5)	2.459(4)
Zr(1)–Cl(2)	2.470(5)	Zr(2)–Cl(4)	2.473(6)	Zr(3)–Cl(6)	2.464(8)
Zr(1)–C(101)	2.570(18)	Zr(2)–C(201)	2.539(19)	Zr(3)–C(301)	2.501(17)
Zr(1)–C(102)	2.490(22)	Zr(2)–C(202)	2.517(20)	Zr(3)–C(302)	2.470(18)
Zr(1)–C(103)	2.460(22)	Zr(2)–C(203)	2.478(23)	Zr(3)–C(303)	2.478(19)
Zr(1)–C(104)	2.463(25)	Zr(2)–C(204)	2.477(20)	Zr(3)–C(304)	2.466(27)
Zr(1)–C(105)	2.457(53)	Zr(2)–C(205)	2.462(22)	Zr(3)–C(305)	2.533(21)
Zr(1)–C(111)	2.545(17)	Zr(2)–C(211)	2.527(22)	Zr(3)–C(311)	2.525(22)
Zr(1)–C(112)	2.497(21)	Zr(2)–C(212)	2.527(23)	Zr(3)–C(312)	2.482(21)
Zr(1)–C(113)	2.427(24)	Zr(2)–C(213)	2.475(20)	Zr(3)–C(313)	2.486(22)
Zr(1)–C(114)	2.472(23)	Zr(2)–C(214)	2.474(20)	Zr(3)–C(314)	2.500(29)
Zr(1)–C(115)	2.476(19)	Zr(2)–C(215)	2.468(22)	Zr(3)–C(315)	2.494(22)
Zr(1)–Cp(1) [a]	2.196	Zr(2)–Cp(3)	2.200	Zr(3)–Cp(5)	2.190
Zr(1)–Cp(2)	2.180	Zr(2)–Cp(4)	2.214	Zr(3)–Cp(6)	2.198
Bond angles (°)					
Cl(1)–Zr(1)–Cl(2)	94.2(2)	Cp(1)–Zr(1)–Cp(2)	133.7		
Cl(30–Zr(2)–Cl(4)	95.1(2)	Cp(3)–Zr(2)–Cp(4)	131.5		
Cl(5)–Zr(3)–Cl96)	94.2(2)	Cp(50–Zr(3)–Cp(6)	130.1		

[a] Cp is the centre of the cyclopentadienyl ring.

uration was determined by Hope's method [11] using the anomalous scattering of zirconium atom for Cu-K_α radiation, with the (*R*,*R*)-structure coordinations and $\Delta f'' = -2.245, 0, -2.245$, respectively. After 12 cycles of least-squares refinement, the *R* factors converged to 0.0645, 0.0668, 0.0726, respectively, indicating unambiguously (*R*,*R*)-configuration.

The molecular structures of complexes (*R*,*R*)-**1** and (*R*,*R*)-**3** are shown in Fig. 1. Atomic coordinates and temperature factors are listed in Table 5 and 6, respectively. Hydrogen atomic coordinates, isotropic temperature factors and structure factors of both complexes are available from the authors. Selected bond lengths and angles for complexes *R*,*R*-**1** and *R*,*R*-**3** are listed in Tables 3 and 4.

Results and discussion

The synthetic route is outlined as follows:

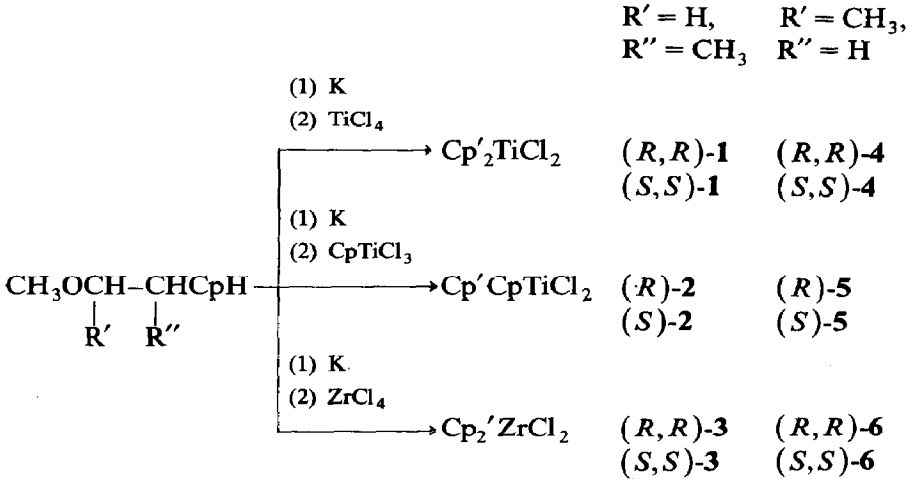

Table 5

Atom coordinates ($\times 10^4$) and temperature factors ($\times 10^3$) for crystal (*R*,*R*)-**1**. (U_{eq}) is defined as 1/3 of the trace of the orthogonalised *U* tensor)

Atom	*x*	*y*	*z*	U_{eq}
Ti(1)	0	0	0	30(1)
Cl(1)	−959(3)	2923(3)	−9(1)	45(1)
Cl(2)	−3880(3)	−2930(3)	9(1)	44(1)
O(1)	−725(12)	2168(11)	−1377(2)	89(4)
O(2)	−2908(13)	−2192(14)	1374(3)	92(5)
C(101)	−453(13)	−126(12)	−690(2)	44(4)
C(102)	1063(15)	1807(15)	−594(3)	49(5)
C(103)	3066(12)	1217(12)	−420(2)	50(4)
C(104)	1942(16)	−1152(15)	−407(3)	50(5)
C(105)	−196(16)	−1991(15)	−565(3)	51(5)
C(106)	−2537(16)	−276(17)	−866(3)	75(6)
C(107)	−3743(19)	−2364(19)	−1122(4)	117(7)
C(108)	−2032(21)	1900(24)	−1071(3)	108(9)
C(109)	−136(22)	4302(18)	−1558(4)	124(8)
C(111	−318(13)	139(12)	688(2)	44(4)
C(112)	−230(14)	−1851(12)	592(2)	49(4)
C(113)	1862(13)	−1197(13)	423(2)	53(4)
C(114)	3112(13)	1177(13)	416(3)	54(4)
C(115)	1779(14)	2003(13)	575(2)	54(4)
C(116)	−2208(16)	358(16)	870(3)	73(6)
C(117)	−1324(23)	2412(17)	1119(3)	114(9)
C(118)	−3923(17)	−1832(22)	1068(3)	99(7)
C(119)	−4392(22)	−4310(16)	1565(4)	123(8)
Ti(2)	2551(2)	−3728(2)	−3332(1)	30(1)
Cl(3)	6420(3)	−2777(3)	−3341(1)	43(1)
Cl(4)	3505(3)	152(3)	−3323(1)	45(1)
O(3)	3274(15)	−819(14)	−1961(3)	90(5)
O(4)	5420(12)	−3018(11)	−4703(2)	94(4)
C(201)	3020(13)	−3391(11)	−2647(2)	42(4)
C(202)	949(13)	−3499(12)	−2739(2)	48(4)
C(203)	−511(14)	−5577(13)	−2913(2)	54(4)
C(204)	627(13)	−6826(11)	−2919(2)	53(4)
C(205)	2780(13)	−5512(12)	−2767(2)	51(4)
C(206)	5095(15)	−1452(15)	−2465(3)	74(5)
C(207)	6335(18)	−2341(21)	−2214(4)	116(8)
C(208)	4635(23)	218(17)	−2268(3)	101(7)
C(209)	2688(23)	691(22)	−1771(4)	120(9)
C(211)	2870(13)	−3258(12)	−4018(2)	47(4)
C(212)	778(13)	−3521(12)	−3909(2)	51(4)
C(213)	−577(14)	−5669(13)	−3740(2)	52(4)
C(214)	710(15)	−6769(11)	−3756(2)	54(4)
C(215)	2787(13)	−5343(12)	−3923(2)	49(4)
C(216)	4768(17)	−1141(15)	−4204(3)	70(5)
C(217)	3860(23)	−1(16)	−4451(3)	120(8)
C(218)	6445(18)	−1627(16)	−4398(3)	99(6)
C(219)	6936(21)	−3602(18)	−4897(4)	124(8)
Ti(3)	6268(2)	3720(2)	−6667(1)	30(1)
Cl(5)	3353(3)	−151(3)	−6674(1)	44(1)
Cl(6)	9197(3)	2770(3)	−6658(1)	44(1)
O(5)	8462(12)	3035(12)	−5294(2)	92(4)
O(6)	4082(12)	833(10)	−8040(2)	93(4)
C(301)	6140(14)	3261(12)	−5985(2)	45(4)

Table 5 (continued)

Atom	x	y	z	U_{eq}
C(302)	8111(14)	5326(12)	−6075(2)	47(4)
C(303)	7452(15)	6765(11)	−6247(2)	52(4)
C(304)	5091(15)	5652(12)	−6262(2)	49(4)
C(305)	4257(14)	3510(13)	−6100(2)	53(4)
C(306)	5956(20)	1176(15)	−5795(3)	70(6)
C(307)	3913(20)	−64(16)	−5551(3)	110(7)
C(308)	8101(22)	1670(17)	−5607(3)	95(8)
C(309)	10548(20)	3631(18)	−5104(4)	127(8)
C(311)	6435(14)	3410(12)	−7350(2)	43(4)
C(312)	8279(13)	5516(12)	−7234(2)	46(4)
C(313)	7436(15)	6823(12)	−7066(2)	49(4)
C(314)	5088(14)	5594(12)	−7089(2)	51(4)
C(315)	4428(14)	3477(13)	−7256(2)	50(4)
C(316)	6582(18)	1463(14)	−7536(3)	72(6)
C(317)	8646(20)	2309(21)	−7781(4)	120(9)
C(318)	4441(23)	−203(16)	−7724(3)	96(8)
C(319)	1962(20)	−674(21)	−8223(4)	129(8)

The chiral cyclopentadienes are prepared as described in ref. 12. The properties of the chiral cyclopentadienyl complexes are listed in Table 1. The titanium and zirconium atoms in both complexes are surrounded by two cyclopentadienyl rings and two chlorine atoms. The ethereal oxygen atom in the side chain does not coordinate to the metal atom. It is very similar to those in $(CH_3OCH_2CH_2Cp)_2TiCl_2$ [13]. However, it is likely that in the catalytic intermediate [Cp'_2TiH], which is formed in situ from Cp'_2TiCl_2 and i-C_3H_7MgBr [14], the ethereal oxygen atom of the side chain on the cyclopentadienyl ring could coordinate to the titanium atom to form a chelate ring. Because the titanium atom in low-valent species can accept the coordination of an ethereal oxygen atom [15,16], or a PMe_3 ligand [17], if the geometry of the ligand allows itself to form a chelate ring, we believe that the formation of a chelate ring in the catalytic intermediate [Cp'_2TiH] is possible. In the complexes $CH_3OCH_2CH_2CpTiCl_3$ and (cyclo-$C_4H_7OCH_2Cp$)$TiCl_3$, the structural evidence for Ti–O coordination has been obtained [13]. Such a ring will bring the chiral atom near to the reaction center of the catalyst molecule, and probably leading to higher enantiomeric excesses. Asymmetric catalysis studies using such complexes as catalysts are currently in progress.

Table 6

Atom coordinates ($\times 10^4$) and temperature factors ($\times 10^3$) for crystal (*R*,*R*)-**3**. (U_{eq} is defined as 1/3 of the trace of the orthogonalised U tensor)

Atom	x	y	z	U_{eq}
Zr(1)	0	0	0	28(1)
Cl(1)	−917(11)	3036(8)	−6(2)	50(3)
Cl(2)	−3994(10)	−3054(9)	6(2)	49(3)
O(1)	−611(37)	2123(32)	−1386(6)	104(13)
O(2)	−2864(42)	−2184(33)	1378(6)	113(15)
C(101)	−376(28)	−76(33)	−712(5)	39(11)
C(102)	1638(35)	1808(32)	−610(6)	50(13)
C(103)	3102(34)	1189(31)	−451(6)	55(12)
C(104)	1966(34)	−1211(34)	−437(6)	51(13)
C(105)	−161(31)	−1951(31)	−583(6)	50(11)
C(106)	−2399(42)	−164(55)	−892(7)	100(24)
C(107)	−3845(46)	−2179(53)	−1141(10)	145(22)
C(108)	−1855(69)	1993(60)	−1083(9)	138(33)
C(109)	−105(77)	4344(54)	−1571(11)	162(30)
C(111)	−223(33)	138(33)	706(5)	61(14)
C(112)	−121(36)	−1801(31)	611(6)	45(12)
C(113)	1916(33)	−1183(32)	437(5)	46(12)
C(114)	3196(36)	1210(32)	437(7)	53(12)
C(115)	1814(37)	1968(31)	587(6)	52(13)
C(116)	−2150(34)	234(32)	881(5)	76(17)
C(117)	−1514(67)	2189(48)	1137(9)	156(32)
C(118)	−3854(53)	−1851(50)	1078(10)	137(28)
C(119)	−4490(72)	−4309(50)	1565(11)	154(28)
Zr(2)	2816(3)	−3598(3)	−3333(1)	29(1)
Cl(3)	6758(10)	−2676(9)	−3342(2)	49(3)
Cl(4)	3685(10)	378(8)	−3326(2)	45(3)
O(3)	3443(36)	−820(36)	−1949(6)	93(13)
O(4)	5663(43)	−2911(38)	−4711(6)	106(16)
C(201)	3062(30)	−3338(33)	−2629(5)	44(12)
C(202)	1132(34)	−3467(32)	−2718(5)	51(12)
C(203)	−376(42)	−5530(37)	−2892(6)	61(15)
C(204)	804(38)	−6734(35)	−2885(6)	55(14)
C(205)	2911(34)	−5411(33)	−2747(6)	49(12)
C(206)	5111(38)	−1397(37)	−245(6)	101(18)
C(207)	6337(47)	−2270(47)	−2210(8)	123(21)
C(208)	4563(64)	192(42)	−2244(7)	177(28)
C(209)	2948(65)	927(22)	−1813(11)	162(29)
C(211)	2951(33)	−3249(29)	−4034(6)	56(13)
C(212)	951(36)	−3553(31)	−3938(6)	59(13)
C(213)	−390(37)	−5617(34)	−3769(5)	50(12)
C(214)	864(38)	−6733(33)	−3783(6)	42(12)
C(215)	2876(45)	−5280(33)	−3938(6)	52(15)
C(216)	4912(35)	−1218(32)	−4227(5)	86(16)
C(217)	4086(58)	45(58)	−4458(10)	147(27)
C(218)	6545(38)	−1733(46)	−4413(7)	109(18)
C(219)	7187(61)	−3495(59)	−4895(10)	133(26)
Zr(3)	5403(4)	3598(3)	−6667(1)	29(1)
Cl(5)	3368(9)	−379(8)	−6674(2)	44(3)
Cl(6)	9436(9)	2682(9)	−6658(2)	46(3)
O(5)	8673(39)	2974(33)	−5293(6)	107(14)
O(6)	4205(37)	798(34)	−8031(6)	100(13)
C(301)	6073(33)	3222(26)	−5975(5)	51(11)
C(302)	8140(34)	5286(30)	−6062(5)	48(11)

Table 6 (continued)

Atom	x	y	z	U_{eq}
C(303)	7544(33)	6721(29)	−6215(5)	41(11)
C(304)	5207(38)	5600(33)	−6234(7)	61(14)
C(305)	4359(33)	3505(30)	−6074(5)	48(11)
C(306)	6043(36)	1194(35)	−5784(6)	75(17)
C(307)	4024(51)	−146(48)	−5534(8)	111(22)
C(308)	8188(46)	1639(47)	−5597(8)	119(26)
C(309)	10813(52)	3583(57)	−5138(12)	159(24)
C(311)	6353(35)	3382(31)	−7369(6)	53(13)
C(312)	8324(38)	5457(33)	−7257(6)	55(13)
C(313)	7575(40)	6782(36)	−7118(8)	136(29)
C(314)	5196(58)	5563(33)	−7115(7)	76(15)
C(315)	4544(37)	3467(33)	−7271(6)	58(12)
C(316)	6507(35)	1442(32)	−7538(6)	90(19)
C(317)	8436(49)	2064(57)	−7788(8)	136(29)
C(318)	4496(58)	−216(44)	−7752(9)	152(30)
C(319)	1974(55)	−777(51)	−8209(10)	138(23)

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