Crystal structure of enantiomerically pure bis(dimethylbicyclooctylcyclopentadienyl)zirconium dichloride

Ronald L. Halterman *, Zhouliang Chen

Department of Chemistry and Biochemistry, The University of Oklahoma, 620 Parrington Oval, Norman, OK 73019-0370, USA

Abstract

The enantiomerically pure C_2-symmetrical $(DMeBCOCp)_2ZrCl_2$ complex (+)-3 was synthesized from enantiomerically pure (−)-DMeBCOCp ligand (−)-1. Zirconocene (+)-3 was recrystallized from toluene to provide single crystals suitable for X-ray diffraction. The unit cell contained two conformationally similar molecules in the monoclinic space group P2₁ (#4), a = 7.288(4) Å, b = 18.980(2) Å, c = 17.612(3) Å, β = 91.43(2)°, V = 2436(1) Å³, Z = 4. Of the 7247 unique reflections, 5691 observed reflections (3σ or greater) were refined to give a final R = 0.048 and Rw = 0.061. The cyclopentadienyl substituents are arranged in a roughly C_2-symmetrical orientation and the cyclopentadienyl carbons are close to a synclinal orientation.

1. Introduction

In the past several years an impressive number of new chiral metallocene complexes have been reported [1]. While chiral ansa-metallocenes are more common [1,2], recent interest is being focused on conformational mobility in unbridged zirconocene catalysts for propene polymerization [3]. Such complexes can switch between C_2-symmetrical and unsymmetrical conformations, leading to potentially interesting reactivity. By utilizing hindered chiral unbridged complexes, a particular conformation may be favored and the rate of conformational switching may be altered, which could lead to selective and novel reactivity. One example is the high enantioselectivity exhibited by a bis(diphenylbicyclooctylcyclopentadienyl)titanium complex in catalyzing enantioselective hydrogenations [5]. We have previously reported the synthesis and crystal structure of a second BCOCp–titanium complex, the bis(dimethylbicyclooctylcyclopentadienyl)titanium dichloride 2 [6]. However, no crystal structures of analogous zirconium complexes have been reported. Given the interest in un-

bridged zirconocene complexes and the desire to learn more about their conformational preferences, we have isolated single crystals of enantiomerically pure bis(dimethylbicyclooctylcyclopentadienyl)zirconium dichloride (+)-3 and now report its X-ray diffraction-derived crystal structure.

2. Zirconium complexes

The enantiomerically pure C_2-symmetrical (DMeBCOCp)₂ZrCl₂ complex (+)-3 was synthesized from enantiomerically pure (−)-DMeBCOCp ligand (−)-1 following our published procedure to give white-yellow crystals of zirconium complex (+)-3 [6]. Since the metalation was performed on a single enantiomer of the DMeBCOCp ligand, only a single C_2-symmetric isomer could be formed. Single crystals were obtained by the slow evaporation of a toluene solution of zirconocene (+)-3, and their X-ray diffraction data were measured. A summary of the data collection and refinement values is given in Table 1. Selected bond lengths, bond angles, torsion angles and positional parameters are given in Tables 2–5.

The non-centrosymmetric monoclinic unit cell (P2₁) of enantiomerically pure zirconium complex (+)-3 con-

---

* Corresponding author.

Table 1

Summary of crystallographic data for (+)-(DMeBCOCp)$_2$-ZrCl$_2$(+)-(3)

Empirical formula	C$_{26}$H$_{34}$Cl$_2$Zr
F.W.	508.68
Cryst syst	Monoclinic
Space group	P2$_1$ (#4)
Cryst size (mm)	0.20×0.10×0.06
Cryst color, habit	Colorless, plate
Cell dimens	25 rflns, 25° ≤ 2θ ≤ 50°
a (Å)	7.288(4)
b (Å)	18.980(2)
c (Å)	17.612(3)
β (deg)	91.43(2)
V (Å^3)	2436.3(1.3)
Z	4
d(calc) (g cm^{-3})	1.387
Abs coeff (cm^{-1})	58.77
T (K)	293
Diffractometer	Rigaku AFC5R
Radiation	CuKα (λ = 1.54178 Å)
Monochromator	Graphite
Scan limit (deg)	5 ≤ 2θ ≤ 120
Scan speed (deg min^{-1})	32
Data collected	h 0–8, k ±21, l ±20
No. of frlns collected	7884
No. of unique rflns	7247
No. of obs. reflns (≥ 3σ)	5691
Rint	0.036
Abs cor (trans. factors)	0.61–1.00
Structure soln	Direct method (TEXSAN)
Refinement	Least squares
R	0.048
Rw	0.061
GOF	2.17
Max param shift/esd	0.13
Max resid e density (e Å^{-3})	1.13 (−1.03)

tained two crystallographically independent but conformationally similar molecules; Fig. 1 shows an ORTEP of one of the molecules. Similar to the case of the titanium complex (−)-2, the DMeBCOCp ligands in each of the independent molecules of complex (+)-3 adopt a synclinal arrangement, with the shortest intramolecular contacts lying between C(2)–C(15) (3.267 Å), C(2)–C(16) (3.298 Å) and C(3)–C(15) (3.407 Å), and the biclyclooctane moieties are oriented in a nearly C$_2$-symmetrical conformation, with the methyl groups on the bicyclooctane framework located away from the chlorine ligands. The Zr–C (η^5) distances fall in the range of 2.44–2.66 Å, with the same variation order as in the titanium complex (−)-2. The bicyclooctane framework is bent away from the ZrCl$_2$ moiety and is distorted, though to a lesser extent than the titanium complex (−)-2 (bonds C(6)–C(7) or C(1)–C(2) out of the attached Cp plane by 14.4 or 23°; angles C(6)–C(7)–C(11) = 108.6° and C(2)–C(1)–C(10) = 114.4° for 3 vs. C(6)–C(7)–C(8) = 104.7° and C(2)–C(1)–C(9) = 101.5°; torsion angles C(7)–C(11)–C(10)–C(13) = −147° vs. C(1)–C(9)–C(8)–C(12) = −142°) for 2. The Cl–Zr–Cl angle (94.1°) is quite normal. Both cyclopentadienyl rings in (+)-3 encompass coplanar ring carbons with a deviation of less than 1°, but the substituted carbon–Zr distances in one of the cyclopentadienyl rings are substantially different (C(15) at 2.58 Å and C(19) at 2.66 Å). These diminished structural variations relative to titanium complex 2 are in keeping with the longer Zr–C (η^5) bond which should result in less steric hindrance between the ZrCl$_2$ and the BOCp moieties.

An interesting feature of this structure is that the orientation of the bicyclooctane rings in (+)-3 is quite similar to the C$_2$-symmetric orientation of the rings in an ansa-metallocene, ethano-bridged bis(tetrahydroindenyl)zirconium dichloride [7]. Owing to the lack of coalescence in the low temperature ^{1}H NMR specta of 3, no evidence for multiple static conformations of 3 was found. The structural information presented here should aid in the interpretation of future stereoselective reactions of (+)-3.
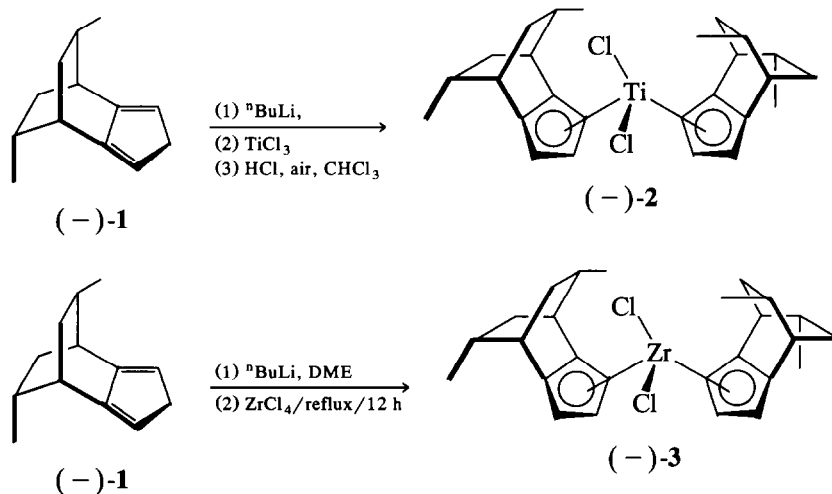

(−)-1   (1) ^{n}BuLi, (2) TiCl$_3$ (3) HCl, air, CHCl$_3$ → (−)-2

(−)-1   (1) ^{n}BuLi, DME (2) ZrCl$_4$/reflux/12 h → (−)-3

Table 2
Selected bond lenghts for (+)-3

Atom	Atom	Distance
ZR	CL1	2.446(3)
ZR	CL2	2.439(3)
ZR	C2	2.605(9)
ZR	C3	2.499(9)
ZR	C4	2.436(8)
ZR	C5	2.492(3)
ZR	C6	2.604(9)
ZR	C15	2.582(9)
ZR	C16	2.487(9)
ZR	C17	2.443(9)
ZR	C18	2.523(9)
ZR	C19	2.659(8)
C1	C2	1.53(1)
C1	C9	1.56(1)
C1	C10	1.54(1)
C2	C3	1.38(1)
C3	C4	1.42(1)
C4	C5	1.39(1)
C5	C6	1.49(1)
C6	C7	1.49(1)
C7	C11	1.53(2)
C14	C15	1.53(1)
C14	C22	1.53(1)
C14	C23	1.52(1)
C15	C16	1.40(1)
C15	C19	1.42(1)
C16	C17	1.43(1)
C17	C18	1.43(1)
C18	C19	1.40(1)
C19	C20	1.49(1)
C20	C21	1.54(1)
C20	C24	1.52(1)
ZR(B)	CL1(B)	2.437(3)
ZR(B)	CL2(B)	2.433(3)
ZR(B)	C2(B)	2.586(8)
ZR(B)	C3(B)	2.487(7)
ZR(B)	C4(B)	2.427(8)
ZR(B)	C5(B)	2.517(8)
ZR(B)	C6(B)	2.616(8)
ZR(B)	C15(B)	2.616(8)
ZR(B)	C16(B)	2.509(8)
ZR(B)	C17(B)	2.448(8)
ZR(B)	C18(B)	2.486(9)
ZR(B)	C19(B)	2.598(8)

Table 3
Selected bond angles for (+)-3

Atoms			Angle
1	2	3	
CL1	ZR	CL2	94.1(1)
C2	ZR	C19	129.9(3)
C3	ZR	C18	134.4(3)
C4	ZR	C17	145.5(3)
C5	ZR	C16	132.1(3)
C6	ZR	C15	129.7(3)
C2	C1	C9	101.5(7)
C2	C1	C10	114.4(8)
C9	C1	C10	106.5(8)
C1	C2	C3	132.8(8)
C1	C2	C6	112.9(8)
C3	C2	C6	108.6(8)
C2	C3	C4	108.4(8)
C3	C4	C5	106.4(8)
C4	C5	C6	108.9(8)
C2	C6	C5	107.6(8)
C2	C6	C7	114.8(8)
C6	C6	C7	135.4(8)
C6	C7	C8	104.7(8)
C6	C7	C11	108.6(8)
C8	C7	C11	107.5(1)
C7	C8	C12	114(1)
C1	C10	C13	114.8(8)
CL1(B)	ZR(B)	CL2(B)	93.0(2)
CL2(B)	ZR(B)	C19(B)	131.0(2)
CL3(B)	ZR(B)	C18(B)	132.6(3)
CL4(B)	ZR(B)	C17(B)	144.1(3)
CL5(B)	ZR(B)	C16(B)	135.3(3)
CL6(B)	ZR(B)	C15(B)	130.6(2)

3. Experimental details

3.1. (+)-Bis-[(1S,7S,8R,10R)-8,10-dimethyltricyclo-[5.2.2.02,6]- 2,5-undecadienyl]zirconium dichloride [(+)-(DMeBCOCp)2ZrCl2, (+)-3] [6]

To DMeBCOCp diene (−)-1 (348 mg, 2 mmol) in DME (10 ml) in a 25 ml flask was added dropwise at

Table 4
Selected torison angles for (+)-3

Atoms				Angle	Atoms				Angle
1	2	3	4		1	2	3	4	
C1	C2	C6	C5	157.0(8)	C2	C6	C5	C4	0(1)
C3	C2	C6	C7	−165.6(8)	C4	C3	C2	C6	0(1)
C1	C9	C8	C12	−142(1)	C18	C17	C16	C15	1(1)
C7	C11	C10	C13	−147(1)	C16	C17	C18	C19	1(1)

Table 5
Positional parameters and B(eq) for (+)-3

| Atom	x	y	z	B (eq)
Zr	0.32587(8)	0.6458	0.2146(4)	5.23(3)
Cl(1)	0.1422(4)	0.6924(1)	0.1076(2)	8.8(2)
Cl(2)	0.0595(4)	0.6111(2)	0.2867(2)	9.8(2)
C(1)	0.662(1)	0.6871(5)	0.3861(5)	6.1(5)
C(2)	0.545(1)	0.7038(4)	0.3154(5)	4.7(4)
C(3)	0.587(1)	0.7273(4)	0.2441(5)	4.7(4)
C(4)	0.436(1)	0.7669(4)	0.2146(5)	4.9(4)
C(5)	0.304(1)	0.7660(4)	0.2701(6)	5.9(5)
C(6)	0.370(1)	0.7273(4)	0.3323(6)	5.5(4)
C(7)	0.323(1)	0.7215(6)	0.4141(6)	7.1(6)
C(8)	0.458(2)	0.7731(6)	0.4564(6)	7.4(6)
C(9)	0.660(2)	0.7592(6)	0.4290(6)	7.3(6)
C(10)	0.578(1)	0.6325(6)	0.4396(5)	7.1(5)
C(11)	0.368(1)	0.6466(8)	0.4417(6)	8.7(6)
C(12)	0.404(2)	0.8501(7)	0.4502(7)	9.2(7)
C(13)	0.623(2)	0.5569(7)	0.4219(6)	8.9(7)
C(14)	0.710(1)	0.5875(5)	0.0801(5)	5.1(4)
C(15)	0.566(1)	0.5758(4)	0.1399(5)	4.8(4)
C(16)	0.576(1)	0.5568(4)	0.2169(5)	4.4(4)
C(17)	0.408(2)	0.5224(5)	0.2354(6)	6.0(5)
C(18)	0.301(1)	0.5208(4)	0.1663(7)	5.9(5)
C(19)	0.397(1)	0.5516(4)	0.1072(5)	4.9(4)
C(20)	0.395(1)	0.5483(5)	0.0224(6)	6.7(5)
C(21)	0.542(2)	0.4924(5)	0.0052(5)	6.8(5)
C(22)	0.724(1)	0.5150(5)	0.0447(5)	6.1(5)
C(23)	0.648(1)	0.6384(6)	0.0178(4)	5.9(4)
C(24)	0.455(1)	0.6176(5)	−0.0124(6)	6.9(5)
C(25)	0.489(2)	0.4166(6)	0.0274(8)	9.5(8)
C(26)	0.656(1)	0.7161(5)	0.0375(7)	7.1(6)
Zr((B))	−0.10444(8)	0.63992(6)	0.72727(4)	4.90(3)
Cl(1(B))	−0.3002(4)	0.5702(2)	0.6420(2)	10.2(2)
Cl(2(B))	−0.3642(4)	0.6900(2)	0.7925(2)	10.7(2)
C(1(B))	0.274(1)	0.4973(5)	0.7300(6)	5.8(5)
C(2(B))	0.138(1)	0.5458(4)	0.7650(5)	4.4(4)
C(3(B))	0.157(1)	0.6046(4)	0.8123(5)	4.6(4)
C(4(B))	−0.006(1)	0.6075(4)	0.8552(5)	5.4(4)
C(5(B))	−0.121(1)	0.5516(5)	0.8335(5)	5.6(5)
C(6(B))	−0.030(1)	0.5130(4)	0.7773(5)	4.7(4)
C(7(B))	−0.044(1)	0.4379(5)	0.7518(6)	6.2(5)
C(8(B))	0.101(2)	0.3985(5)	0.7966(7)	7.4(6)
C(9(B))	0.289(1)	0.4363(5)	0.7876(7)	7.7(6)
C(10(B))	0.204(2)	0.4627(5)	0.6558(7)	7.7(6)
C(11(B))	0.008(2)	0.4336(6)	0.6658(7)	7.8(6)
C(12(B))	0.044(2)	0.3871(6)	0.8785(8)	9.5(8)
C(13(B))	0.217(2)	0.5109(7)	0.5861(6)	8.4(7)
C(14(B))	−0.117(2)	0.8399(6)	0.7281(6)	7.3(6)
C(15(B))	−0.068(1)	0.7717(4)	0.6907(5)	5.0(4)
C(16(B))	−0.142(1)	0.7352(5)	0.6312(6)	5.9(5)
C(17(B))	−0.001(1)	0.6872(5)	0.6063(5)	5.5(4)
C(18(B))	0.149(1)	0.6954(4)	0.6543(5)	5.2(4)
C(19(B))	0.110(1)	0.7490(4)	0.7090(5)	4.7(4)
C(20(B))	0.226(1)	0.8008(5)	0.7501(6)	6.3(5)
C(21(B))	0.142(2)	0.8262(5)	0.8251(7)	8.6(7)
C(22(B))	−0.067(2)	0.8355(6)	0.8147(7)	9.2(8)
C(23(B))	0.013(2)	0.8941(5)	0.6924(8)	8.9(8)
C(24(B))	0.213(2)	0.8664(5)	0.6949(8)	8.6(7)
C(25(B))	0.187(2)	0.7803(5)	0.8935(6)	8.6(7)
C(26(B))	−0.042(2)	0.9136(6)	0.6104(8)	10.0(8)
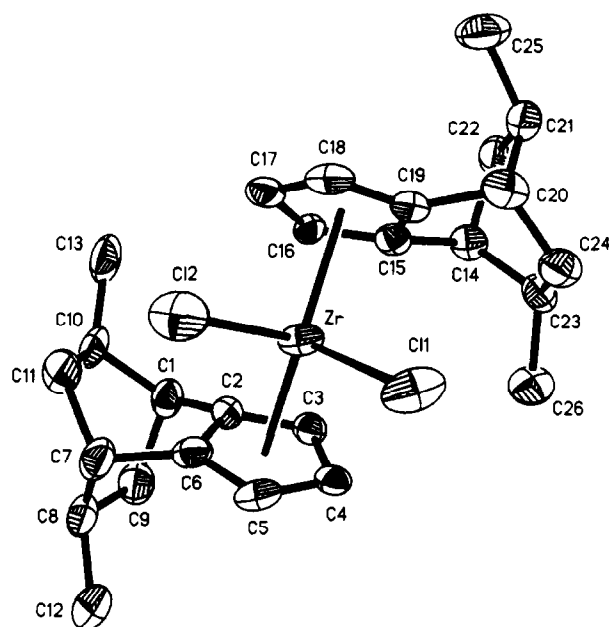
Fig. 1. ORTEP of (+)-3 (50% probability elipsoids). Halterman and Chen structure of $(DiMeBCOCp)_2ZrCl_2$.

−78°C n-butyl lithium (2.2 M in hexane, 1 ml, 2.2 mmol). The resulting mixture was allowed to rise to 0°C and stirred for 30 min, then at room temperature for another 30 min to afford a pink slurry. To a second 50 ml flask containing $ZrCl_4$ (234 mg, 1 mmol), was added at 0°C the precooled (0°C) lithio salt solution. The resulting yellow slurry was heated at reflux for 12 h. Upon being cooled to room temperature, the solvent was removed in vacuo to give a yellow residue which was extracted with CH_2Cl_2 (2 × 15 ml). Removal of the solvent from the filtrate via rotary evaporation gave a yellow-orange solid (515 mg). A portion (121 mg) of the crude product was sublimed (10^{-4} Torr, 175°C, dry ice–acetone cooling) to afford (+)-3 as yellow crystals (77 mg, 64.5% as the reaction yield): m.p. 229–230°C. $[\alpha]D^{22}$ + 138° (c 0.555, CH_2Cl_2). IR (KBr): 2920, 2860, 1450, 1375, 1150, 1030, 880, 830, 805 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.23 (m, 4 H), 6.10 (m, 2 H), 2.93 (br s, 2 H), 2.77 (br s, 2 H), 1.98 (m, 4 H), 1.85 (m, 4 H), 1.67 (m, 2 H), 1.02 (d, $J = 7.0$ Hz, 6 H), 0.48 (d, $J = 6.5$ Hz, 6 H), 0.20 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.61, 132.70, 117.85, 111.82, 107.85, 42.88, 40.39, 39.03, 34.50, 32.33, 31.04, 21.74, 20.91. MS: m/z (EI, 70 eV, rel. intensity) 510 ($M^+ + 4$, 12%), 509 ($M^+ + 3$, 7), 508 ($M^+ + 2$, 18), 507 ($M^+ + 1$, 8), 506 (M^+, 16), 475 (7), 474 (6), 473 (13), 472 (10), 471 (18), 337 (64), 336 (25), 335 (100), 334 (33), 333 (98). HRMS (EI, 70 eV) calc. for $C_{26}H_{34}ZrCl_2$

506.1081, found 506.1077. Anal. Found: C, 61.37; H, 6.74. $C_{26}H_{34}ZrCl_2$. Calc.: C, 61.24; H, 6.75.

3.2. X-Ray structure determination of (+)-3

Suitable single crystals were grown from toluene by slow evaporation to give zirconocene dichloride **3** as yellow crystals. The intensity data were obtained at 20°C with a Rigaku AFC5R four-circle autodiffractometer system using graphite monochromated Cu K α radiation and a 12 kW rotating-anode generator. The cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 centered reflections in the range $25 \leqslant 2\theta \leqslant 50$. Scans were made at a speed of 32 deg min^{-1} in omega. The weak reflections ($I \leqslant 10.0\sigma$) were rescanned (maximum of two rescans). The intensities of three standard reflections were measured after every 150 reflections and remained constant throughout the data collection; no decay correction was applied. The crystallographic calculations were performed by using the TEXSAN program [8]. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions for the final full-matrix least-squares refinement cycles, but were not refined.

Acknowledgement

References

[1] R.L. Halterman, *Chem. Rev.*, 92 (1992) 965.
[2] (a) M. Burk, S.L. Colletti and R.L. Halterman, *Organometallics*, 10 (1991) 2998; (b) Z. Chen and R.L. Halterman, *J. Am. Chem. Soc.*, 114 (1992) 2276; (c) Z. Chen and R.L. Halterman, *Organometallics*, 13 (1994) 3932; (d) A.L. Rheingold, N.P. Robinson, J. Whelan and B. Bosnich, *Organometallics*, 11 (1992) 1869; (e) T.K. Hollis, A.L. Rheingold, N.P. Robinson, J. Whelan and B. Bosnich, *Organometallics*, 11 (1992) 2812; (f) M.S. Erickson, F.R. Fronczek and M.L. McLaughlin, *J. Organomet. Chem.*, 415 (1991) 75; (g) J.A. Bandy, M.L.H. Green, I.M. Gardiner and K. Prout, *J. Chem. Soc., Dalton Trans.* (1991) 2207; (h) R.B. Grossman, J.-C. Tsai, W.M. Davis, A. Gutiérrez and S.L. Buchwald, *Organometallics*, 13 (1994) 3892.
[3] G. Erker, M. Aulbach, M. Knickmeier, D. Wingermühle, C. Krüger, M. Nolte and S. Werner, *J. Am. Chem. Soc.*, 115 (1993) 4590.
[4] G. Erker, M. Aulbach, C. Krüger and S. Werner, *J. Organomet. Chem.*, 450 (1993) 1.
[5] R.L. Halterman, K.P.C. Vollhardt, M.E. Welker, D. Bläser and R. Boese, *J. Am. Chem. Soc.*, 109 (1987) 8105.
[6] Z. Chen, K. Eriks and R.L. Halterman, *Organometallics*, 16 (1991) 3449.
[7] (a) F.R.W.P. Wild, M. Wasiucionek, G. Huttner and H.H. Brintzinger, *J. Organomet. Chem.*, 288 (1985) 63; (b) S. Collins, B.A. Kuntz, N.J. Taylor and D.G. Ward, *J. Organomet. Chem.*, 342 (1988) 21.
[8] TEXSAN Program, TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.