

Structure of $(\eta^5\text{-C}_5\text{Me}_5)(\eta^8\text{-C}_8\text{H}_8)\text{Zr}$, an aromatic mixed sandwich complex of zirconium(III)

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Abstract

$(\eta^5\text{-C}_5\text{Me}_5)(\eta^8\text{-C}_8\text{H}_8)\text{Zr}$ is isostructural with its titanium analog, it crystallizes in the centric space group, *Pnma*, with (at -140°C) a 10.218(2) Å, b 12.863(4) Å, c 11.650(2) Å, and D_{calc} 1.43 g cm $^{-3}$ for $Z = 4$. The molecule resides on a mirror plane and is disordered. The pentamethylcyclopentadienyl ligand is ordered with one carbon from the ring and one methyl group residing on the mirror plane. The Zr–C(η^5) distances average 2.478(6) Å and the Zr atom is 2.17 Å from the centroid of this plane. There are two orientations of the cyclooctatetraene dianion, one at 36% occupancy which has two carbon atoms on the mirror plane, and a second with 64% occupancy where the mirror plane bisects two C–C bonds. The two sets of Zr–C(η^8) average separations and Zr–centroid(C_8) distances are 2.42(2) and 1.59 Å for the minor orientation and 2.474(6), 1.67 Å for the major form of the COT ring. The centroid(C_5)–Zr–centroid(C_8) angles average 173.8°.

Introduction

The cyclooctatetraene ligand has been shown to exhibit a variety of bonding modes to zirconium [2–8], however, in none of these has a sandwich complex of two planar aromatic rings been observed. In contrast, with the smaller titanium, $(\eta^5\text{-C}_5\text{H}_5)(\eta^8\text{-C}_8\text{H}_8)\text{Ti}$ [9], $(\eta^5\text{-C}_5\text{Me}_5)(\eta^8\text{-C}_8\text{H}_8)\text{Ti}$ [1], $(\eta^5\text{-C}_5\text{H}_5)(\eta^7\text{-C}_7\text{H}_7)\text{Ti}$ [10], and $(\eta^5\text{-C}_5\text{Me}_5)(\eta^7\text{-C}_7\text{H}_7)\text{Ti}$ [1] have been prepared and structurally characterized. We have undertaken the preparation and structural characterization of such a compound of zirconium and present here the structure of the mixed sandwich complex, $(\eta^5\text{-C}_5\text{Me}_5)(\eta^8\text{-C}_8\text{H}_8)\text{Zr}$, the first paramagnetic zirconium(III) compound. The synthesis and extensive spectroscopic characterization have been reported elsewhere [11].

Results and discussion

The molecular structure and atom labelling scheme for the title compound are given in Fig. 1. As discussed in the Experimental section, the COT dianion is disordered about a crystallographic mirror plane which contains the metal atom, one carbon atom of the C_5 ring, and one methyl group. The differences in the two orientations of the C_8 ring are depicted in Fig. 2. The 'a' orientation contains two carbon atoms on the mirror plane (C(1)a, C(5)a) and is the minor form (36% occupancy). In the major form (64% occupancy) the mirror plane bisects two of the C–C bonds (C(1)b–C(1)b' and C(4)b–C(4)b'). In the room temperature determination of the isostructural $(\eta^5-C_5Me_5)(\eta^8-C_8H_8)Ti$ [1], the two orientations refined at 50% occupancy each. The current refinement of the Zr compound was carried out with data collected at $-140^\circ C$ and the presence of disorder was noted from a preliminary data set even at $-162^\circ C$. It is interesting to note that in a related structure, $(\eta^5-C_5Me_5)(\eta^8-C_8H_8)ZrH$ [3], two molecules per asymmetric unit were observed, with one of the major structural differences being the orientation of the C_5 rings with respect to the C_8 rings. One C_5 ring is staggered with respect to the other, perhaps indicating that very small energy differences separate the orientational preferences for these aromatic rings.

The two orientations of the C_8 ring in the title compound are staggered with respect to one another, and as a result the refinement of these atoms is poor and the standard deviations in bond distances and angles (Table 1) are large. The C–C distances and C–C–C bond angles average $1.39(4) \text{ \AA}$ and $134(3)^\circ$, respectively. The Zr–C(η^8) distances average $2.42(2) \text{ \AA}$ for the 'a' orientation and $2.474(6) \text{ \AA}$ for the 'b' orientation. These are equivalent at 3σ and the average of all nine Zr–C(η^8) observations is $2.45(3) \text{ \AA}$.

The two orientations of the C_8 rings are planar to within 0.03 \AA ('a' orientation) and 0.003 \AA ('b'). The C_5 ring is planar to within 0.004 \AA . The

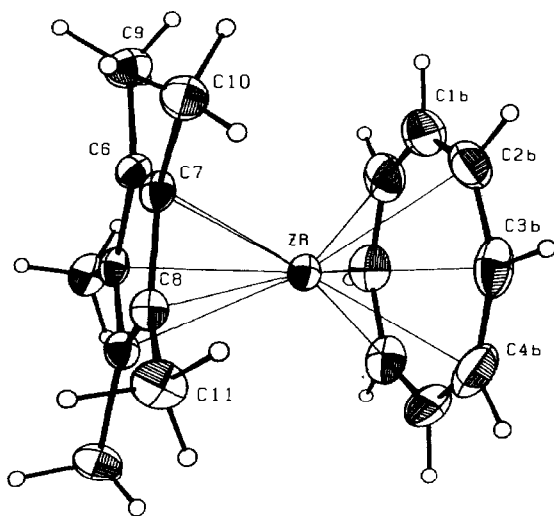


Fig. 1. Molecular structure and atom labelling scheme for $(\eta^5-C_5Me_5)(\eta^8-C_8H_8)Zr$. The 'b' orientation of the COT dianion (64% occupancy) is shown; 50% probability thermal ellipsoids; H atoms arbitrarily reduced.

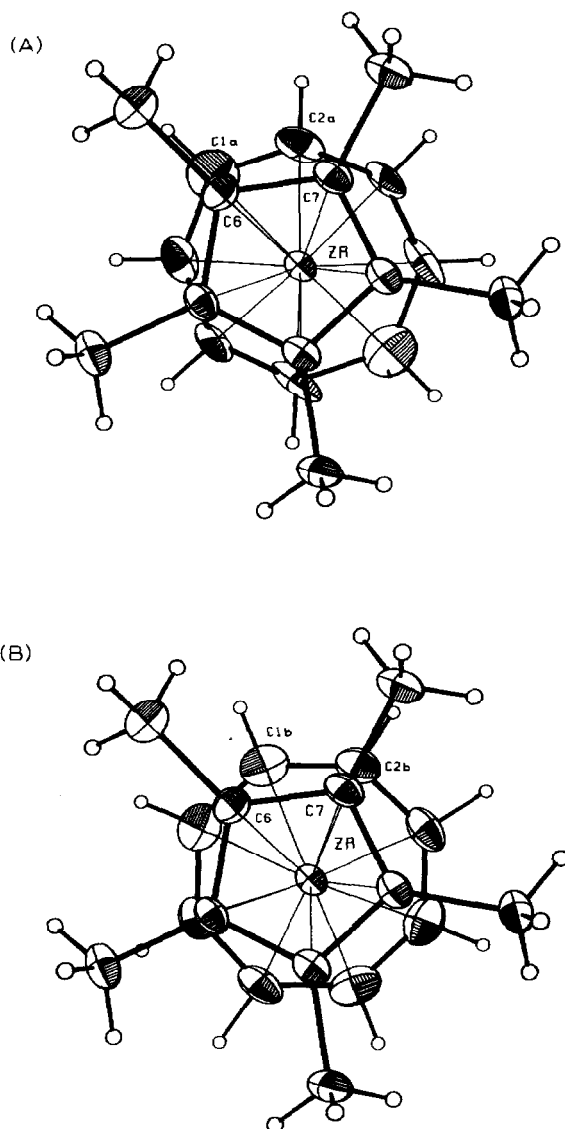


Fig. 2. (A) Top view of the 'a' orientation (34% occupancy); (B) The 'b' orientation (64% occupancy).

centroid(C₈)-Zr-centroid(C₅) angles average 173.8°. This tilt is clearly seen in a side view of the molecule with the major orientation of the C₈ ring (Fig. 3). In contrast this same value for the isostructural Ti complex is much closer to linearity (179°). The latter may be the result of a small steric effect in the compound with the smaller Ti atom. In both the Ti and Zr compounds the C₅ ring is observed to be slightly tilted with the Zr-C(η⁵) distances in the title compound increasing from 2.473(3) Å for C(6) on the mirror to 2.486(2) Å for C(8). The methyl group bonded to C(8), C(11), also exhibits the largest deviation from the plane of the C₅ ring, 0.11 Å away from Zr. The other two unique methyl groups have an average deviation from this plane of 0.06 Å, also away from Zr.

The average Zr-C(η⁵) separation, 2.478(6) Å, is close to the values observed for (η⁵-C₅Me₅)(η⁸-C₃H₈)ZrH [3] (2.51(2) Å) and (η⁵-C₅Me₅)(η³-C₃H₅)(η⁴-C₈H₈)Zr [2]

Table 1

Bond distances (Å) and angles (deg) for $(\eta^5\text{-C}_5\text{Me}_5)(\eta^8\text{-C}_8\text{H}_8)\text{Zr}^a$

Atoms	Distance	Atoms	Distance
Zr–C(1)a	2.45(1)	Zr–C(2)a	2.404(9)
Zr–C(3)a	2.412(7)	Zr–C(4)a	2.419(7)
Zr–C(5)a	2.43(2)		
Zr–C(1)b	2.470(4)	Zr–C(2)b	2.470(4)
Zr–C(3)b	2.485(4)	Zr–C(4)b	2.472(4)
Zr–C(6)	2.473(3)	Zr–C(7)	2.474(2)
Zr–C(8)	2.486(2)		
C(1)a–C(2)a	1.37(1)	C(2)a–C(3)a	1.37(1)
C(3)a–C(4)a	1.37(1)	C(4)a–C(5)a	1.46(1)
C(1)b–C(1)b'	1.35(1)	C(1)b–C(2)b	1.389(6)
C(2)b–C(3)b	1.396(6)	C(3)b–C(4)b	1.413(6)
C(4)b–C(4)b'	1.43(1)		
C(6)–C(7)	1.419(3)	C(6)–C(9)	1.513(5)
C(7)–C(8)	1.410(3)	C(7)–C(10)	1.504(3)
C(8)–C(8)'	1.421(4)	C(8)–C(11)	1.507(4)
Zr–Centa	1.59	Zr–Centb	1.67
Zr–Cent2	2.17		
Atoms	Angle	Atoms	Angle
C(2)a–C(1)a–C(2)a'	131(2)	C(1)a–C(2)a–C(3)a	137.4(9)
C(2)a–C(3)a–C(4)a	136.9(7)	C(3)a–C(4)a–C(5)a	135.2(9)
C(4)a–C(5)a–C(4)a'	129(2)		
C(1)b'–C(1)b–C(2)b	135.7(3)	C(1)b–C(2)b–C(3)b	136.1(4)
C(2)b–C(3)b–C(4)b	133.2(4)	C(3)–C(4)b–C(4)b'	135.0(3)
C(7)–C(6)–C(7)'	107.9(3)	C(7)–C(6)–C(9)	126.0(1)
C(6)–C(7)–C(8)	108.0(2)	C(6)–C(7)–C(10)	125.7(2)
C(8)–C(7)–C(10)	126.3(2)	C(7)–C(8)–C(8)'	108.1(1)
C(7)–C(8)–C(11)	126.8(2)	C(8)–C(8)–C(11)	125.0(1)
Centa–Zr–Cent2	173.9	Centb–Zr–Cent2	173.6

^a Primed atoms are related to those in Table 3 by the crystallographic mirror plane. Centa and b refer to the centroid of the two forms of the C₈ ring; Cent2 to the C₅ ring.

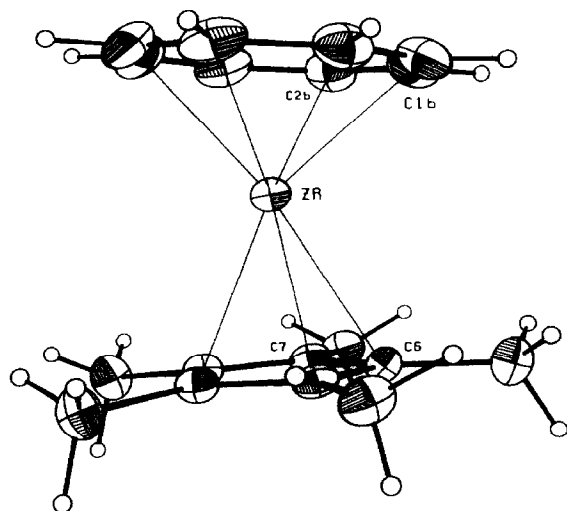


Fig. 3. Side view with the 'b' orientation.

(2.51(1) Å). The average of all nine Zr–C(η^8) distances, 2.45(3) Å, is within the range observed for other η^8 -C₈H₈ compounds of Zr, including (η^8 -C₈H₈)(η^4 -C₈H₈)Zr·THF [5] (2.46(7) Å), (η^8 -C₈H₈)ZrCl₂·THF [6] (2.46(2) Å) and (η^8 -C₈H₈)(η^3 -C₃H₅)Zr·THF [7] (2.479(6) Å).

The pentamethylcyclopentadienyl moiety itself is normal. The average bonding parameters are C–C = 1.417(5) Å, C–Me = 1.508(4) Å, C–C–C = 108.0(1)°, and C–C–Me = 126.0(6)°.

Finally, a comparison with the recently determined (η^5 -C₅Me₅)(η^7 -C₇H₇)Zr reveals little substantial steric effect of the unpaired e[−] in the title complex. In (η^5 -C₅Me₅)(η^7 -C₇H₇)Zr [12], the Zr–centroid(C₅), distance is 2.17 Å, the Zr–C(η^5) average separation is 2.485(2) Å, the centroid(C₅)–Zr–centroid(C₇) angle is 170.3°, and the average bending of the methyl groups, away from the metal, is 0.048 Å. These same parameters for the title compound are 2.17, 2.478(6), 173.8°, and 0.076 Å, respectively.

Table 2

Crystal data and summary of intensity data collection and structure refinement

Compound	(η^5 -C ₅ Me ₅)(η^8 -C ₈ H ₈)Zr
Color/Shape	red/parallelepiped
Formula weight	330.6
Space group	<i>Pnma</i>
Temperature, °C	−140
Cell constants ^a	
<i>a</i> , Å	10.218(2)
<i>b</i> , Å	12.863(4)
<i>c</i> , Å	11.650(2)
Cell volume, Å ³	1531.2
Formula units/unit cell	4
<i>D</i> _{calc} , g cm ^{−3}	1.43
μ _{calc} , cm ^{−1}	6.90
Diffractometer/Scan	Enraf–Nonius CAD-4/ θ –2 θ
Range of relative transmission factors, %	87/100
Radiation, graphite monochromator	Mo- <i>K</i> _α (λ 0.71073 nm)
Max crystal dimensions, mm	0.18 × 0.30 × 0.70
Scan width	0.80 + 0.35 tan θ
Standard reflections	800; 0,14,0; 006
Decay of standards	±1%
Reflections measured	1611
2 θ range, deg	2 ≤ 2 θ ≤ 50
Range of <i>h</i> , <i>k</i> , <i>l</i>	+12, +15, +13
Reflections observed [<i>F</i> _o ≥ 5σ(<i>F</i> _o)] ^b	1260
Computer programs ^c	SHELX[13]
Structure solution	Coordinates from M = Ti[1]
Number of parameters varied	162
Weights	[σ(<i>F</i> _o) ² + 0.004 <i>F</i> _o ²] ^{−1}
GOF	0.67
<i>R</i> = Σ <i>F</i> _o − <i>F</i> _c /Σ <i>F</i> _o	0.034
<i>R</i> _w	0.048
Largest feature final difference map	0.3e [−] Å ^{−3}

^a Least-squares refinement of ((sin θ)/λ)² values for 25 reflections $\theta > 20^\circ$. ^b Corrections: Lorentz-polarization and absorption (empirical, psi scan). ^c Neutral scattering factors and anomalous dispersion corrections from ref. 14.

Experimental

X-ray data collection, structure determination, and refinement for $(\eta^5\text{-C}_5\text{Me}_5)(\eta^8\text{-C}_8\text{H}_8)\text{Zr}$. A red single crystal of the title complex was mounted on a pin and transferred to the goniometer. The crystal was cooled to -140°C during data collection using a stream of cold nitrogen gas. The space group was determined to be either the centric *Pnma* or acentric *Pn2₁a* (a nonstandard setting of *Pna2₁*) from the systematic absences. Utilizing the fractional coordinates from the isostructural Ti analog [1] the structure was refined in the centric *Pnma*. A summary of data collection parameters is given in Table 2.

As observed for the room temperature determination of $(\eta^5\text{-C}_5\text{Me}_5)(\eta^8\text{-C}_8\text{H}_8)\text{Ti}$, the COT ring was found to be disordered about the mirror plane, one orientation

Table 3

Final fractional coordinates for $(\eta^5\text{-C}_5\text{Me}_5)(\eta^8\text{-C}_8\text{H}_8)\text{Zr}$

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eqv} ^a
Zr	0.36291(3)	0.7500	0.51372(3)	0.019
C(1)a	0.319(2)	0.7500	0.720(1)	0.058
C(2)a	0.3626(8)	0.6528(7)	0.6900(7)	0.040
C(3)a	0.4601(7)	0.6112(5)	0.6237(7)	0.035
C(4)a	0.5565(7)	0.6476(5)	0.5526(9)	0.044
C(5)a	0.600(2)	0.7500	0.516(1)	0.056
C(1)b	0.3356(5)	0.6974(4)	0.7162(4)	0.040
C(2)b	0.4097(4)	0.6201(3)	0.6643(4)	0.035
C(3)b	0.5163(4)	0.6166(3)	0.5894(4)	0.036
C(4)b	0.5930(4)	0.6943(4)	0.5362(4)	0.044
C(6)	0.1308(3)	0.7500	0.4536(4)	0.021
C(7)	0.1892(2)	0.6608(2)	0.4034(2)	0.019
C(8)	0.2818(2)	0.6948(2)	0.3220(2)	0.020
C(9)	0.0215(4)	0.7500	0.5412(4)	0.032
C(10)	0.1528(2)	0.5498(2)	0.4287(3)	0.027
C(11)	0.3597(3)	0.6276(2)	0.2410(3)	0.028
H(1)[C(1)a]	0.246	0.750	0.770	(iso)
H(1)[C(2)a]	0.311	0.600	0.724	(iso)
H(1)[C(3)a]	0.462	0.537	0.629	(iso)
H(1)[C(4)a]	0.606	0.593	0.519	(iso)
H(1)[C(5)a]	0.668	0.750	0.459	(iso)
H(1)[C(1)b]	0.268	0.669	0.763	(iso)
H(1)[C(2)b]	0.399	0.546	0.683	(iso)
H(1)[C(3)b]	0.538	0.534	0.584	(iso)
H(1)[C(4)b]	0.660	0.666	0.489	(iso)
H(1)[C(9)]	-0.072(7)	0.750	0.517(4)	(iso)
H(2)[C(9)]	0.024(3)	0.691(3)	0.585(3)	(iso)
H(1)[C(10)]	0.122(4)	0.537(4)	0.509(3)	(iso)
H(2)[C(10)]	0.228(3)	0.503(3)	0.409(3)	(iso)
H(3)[C(10)]	0.082(3)	0.533(2)	0.386(3)	(iso)
H(1)[C(11)]	0.435(3)	0.659(2)	0.224(3)	(iso)
H(2)[C(11)]	0.309(3)	0.623(2)	0.166(3)	(iso)
H(3)[C(11)]	0.380(3)	0.558(3)	0.271(3)	(iso)

^a *U*_{eqv} is equal to (*U*₁₁ + *U*₂₂ + *U*₃₃)/3. 'a' and 'b' refer to the two orientations of the C₈ ring and these atoms were refined with 36% (a) and 64% (b) occupancies.

having two carbon atoms (C(1)a, C(5)a) on the mirror plane, the other having two carbon-carbon bonds (C(1)b-C(1)b', C(4)b-C(4)b') bisected by the plane. Refinement of the occupancies of the two orientations resulted in 36% occupancy for the 'a' orientation and 64% for 'b'. As observed when studying the Ti analog, high correlations between atoms related by the mirror, a higher *R* factor, and higher esd's when attempting to refine in *Pn2₁a*, effectively ruled out the choice of the acentric space group. Interestingly, a second data set collected at -162°C revealed the continued presence of disorder, a further indication that the disorder is in fact static in nature.

A summary of data collection parameters is given in Table 2. The cyclooctatetraene hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with *B* fixed at 5.5 Å². The methyl hydrogen atoms were located from a difference Fourier map and included with fixed contributions (*B* 5.5 Å²). Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of *R* = 0.034 and *R_w* = 0.048. The final values of the positional parameters are given in Table 3.

Supplementary material. Tables of thermal parameters, least-squares planes results and structure factors. See NAPS document No. 04626 for 8 pages of supplementary material which may be ordered from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance in U.S. funds only, \$7.75 for photocopies or \$4.00 for microfiche. Outside the U.S. and Canada, add postage of \$4.50 for the first 20 pages and \$1.00 for each 10 pages of material thereafter. \$1.50 for microfiche postage.

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