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Tris(trimethylsilylcyclopentadienyl)zirconium Chloride

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Tris(trimethylsilylcyclopentadienyl)zirconium Chloride

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Abstract. The title compound is a bent metallocene with two η^5-cyclopentadienyl ligands and one η^1-cyclopentadienyl ligand. The Zr-C bond length to the η^1-cyclopentadienyl ligand is 2.396(5) Å, and the Zr-Cl bond length is 2.442(1) Å.

Comment. The title compound was synthesized as part of a study of zirconium compounds with multiple cyclopentadienyl rings. Zirconium compounds are known to possess up to three η^5-cyclopentadienyl rings as seen in the crystal structures of tetrakis-cyclopentadienylzirconium (Rogers, Vann Bynum, and Atwood, 1978) and tris-cyclopentadienylzirconium triethylaluminum hydride (Kopf, Vollmer, and Kaminsky, 1980); tris-cyclopentadienylzirconium chloride is also reported to possess three η^5-cyclopentadienyl rings (Strittmatter and Bursten, 1991). Also, the *ansa*-bridged tris(cyclopentadienyl) zirconium and hafnium chlorides possess three η^5-cyclopentadienyl ligands (Diamond, Green, Popham & Chernega, 1993). However, the analogous tris-methylcyclopentadienylzirconium chloride (Etievant, Gautheron, and Tainturier, 1977) is reported to possess two η^5-cyclopentadienyl rings and one η^1-cyclopentadienyl ring. The ^{1}H-NMR spectrum of the title compound revealed only one environment for the trimethylsilyl groups implying that the compound either possess three η^5-ligands or that the compound is fluxional with two η^{5-} and one η^1-ligands which inter convert rapidly on the NMR time scale. To determine which coordination geometry was correct, the crystal structure of $(Me_3SiC_5H_4)_3ZrCl$ was determined.

Atomic parameters are listed in Table 1. A list of selected distances and angles is given in Table 2. An ORTEP (Johnson, 1965) drawing of $(Me_3SiC_5H_4)_3ZrCl$ is given in Figure 1. The Zr-C distances for the η^5-cyclopentadienyl rings vary from 2.488(6) Å for Zr-C3 to 2.591(5) for Zr-C1. While the range of bond distances is larger than that of $(\eta^5\text{-}C_5H_5)_2ZrR_2$ compounds (Rogers, Vann Bynum, Atwood, 1978, and references therein), the range of distances is similar to that found in $(\eta^5\text{-}C_5H_5)_3Zr(\eta^1\text{-}C_5H_5)$. The η^1-cyclopentadienyl ring is planar to within 0.02 Å and has C-C bond distances which are similar to the bond distances in the η^1-cyclopentadienyl of $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}C_5H_5)_2$ (Calderon, Cotton, DeBoer, Takats, 1971). The Zr-C14 distances is similar to the Zr-C(η^1) distance of $(\eta^5\text{-}C_5H_5)_3Zr(\eta^1\text{-}C_5H_5)$ [2.774(6) Å].

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Table 1. Atomic Parameters

$$B_{eq} = 1/3\sum_i\sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

Atom	X	y	Z	Beq(Å^2)
Zr	0.05216(1)	0.91599(1)	0.11225(1)	1.97(1)
Cl	-0.0503(1)	1.0455(1)	0.07707(1)	2.99(3)
Si1	0.2735(1)	0.9552(1)	0.03056(1)	2.61(3)
Si2	-0.2734(1)	0.8864(1)	0.12535(1)	2.65(3)
Si3	0.3432(1)	1.0357(2)	0.22674(1)	3.57(4)
C1	0.1803(4)	0.8687(4)	0.0586(1)	2.3(1)
C2	0.2135(4)	0.8091(4)	0.0890(1)	2.5(1)
C3	0.1282(5)	0.7392(4)	0.0986(2)	2.9(1)
C4	0.0386(4)	0.7551(4)	0.0747(2)	2.9(1)
C5	0.0716(4)	0.8330(5)	0.0502(1)	2.8(1)
C6	-0.1292(4)	0.8857(4)	0.1458(1)	2.2(1)
C7	-0.0604(4)	0.7978(4)	0.1516(1)	2.5(1)
C8	0.0335(5)	0.8270(5)	0.1717(1)	2.9(1)
C9	0.0269(5)	0.9347(5)	0.1785(1)	2.8(1)
C10	-0.0729(4)	0.9717(4)	0.1628(1)	2.2(1)
C11	0.2714(4)	1.0616(4)	0.1833(1)	2.6(1)
C12	0.1888(5)	1.1419(4)	0.1765(2)	2.8(1)
C13	0.1465(5)	1.1297(4)	0.1422(1)	2.6(1)
C14	0.1975(4)	1.0385(4)	0.1260(1)	2.2(1)
C15	0.2770(4)	1.0021(5)	0.1524(1)	2.6(1)
C16	0.2944(5)	0.8883(5)	-0.0130(2)	3.8(1)
C17	0.2107(6)	1.0863(5)	0.0226(2)	3.9(2)
C18	0.4110(5)	0.9657(5)	0.0539(2)	4.1(1)
C19	-0.3281(5)	1.0219(5)	0.1257(2)	3.9(1)
C20	-0.3597(6)	0.7999(6)	0.1547(2)	5.4(2)
C21	-0.2728(5)	0.8313(5)	0.0792(2)	4.0(1)
C22	0.298(1)	0.914(1)	0.2453(4)	6.1(4)

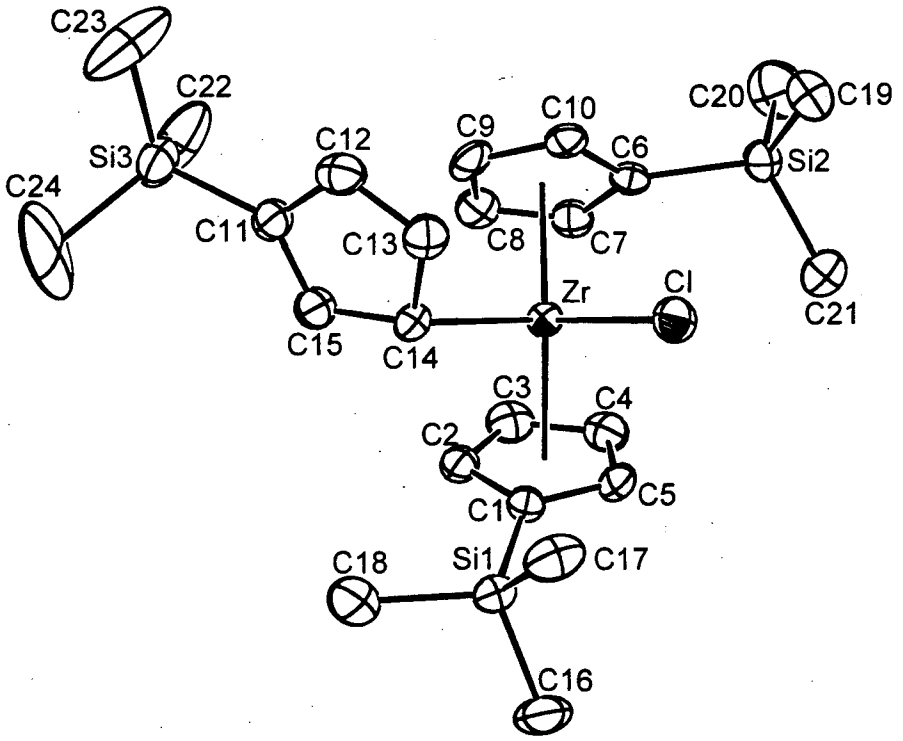
C22`	0.425(1)	1.140(1)	0.2437(4)	5.9(4)
C23	0.310(2)	1.147(1)	0.2574(4)	7.7(5)
C23`	0.433(2)	0.915(1)	0.2218(5)	9.2(5)
C24	0.500(1)	1.037(3)	0.2175(5)	15.4(9)
C24`	0.230(2)	0.998(3)	0.2621(5)	15.1(9)

Table 2. Selected Distances and Angles

Zr - Cl	2.442(1) Å	Zr-C14	2.396(5) Å
Zr-Cp1	2.226 Å	Zr-Cp2	2.194 Å
Zr-C1	2.591(5) Å	Zr-C6	2.536(5) Å
Zr-C2	2.519(5) Å	Zr-C7	2.501(5) Å
Zr-C3	2.488(6) Å	Zr-C8	2.500(5) Å
Zr-C4	2.491(6) Å	Zr-C9	2.500(5) Å
Zr-C5	2.553(r) Å	Zr-C10	2.509(5) Å
C11-C12	1.447(8) Å	C11-C15	1.381(1) Å
C12-C13	1.383(8) Å	C13-C14	1.447(8) Å
C14-C15	1.446(8) Å	Cp(ave)-Zr	2.52(3) Å
Cp1-Zr-Cp2	127.77 °	Cl-Zr-C14	92.1(1) °

Cp1 and Cp2 are the centrolds of the cyclopentadienyl rings.

Figure 1
(Only one set of disordered carbon atoms on Si3 shown)



APPENDIX 2

Experimental form to be completed for each structure (hard-copy submission)

Compound [*e.g.* (1), (2) *etc.*]	
CRYSTAL DATA	
Chemical formula $C_{24}H_{39}Cl\,Si_3Zr$	Crystal system orthorhombic
M_r 538.51	Space group Pbca
a (Å) 11.979 (2)	α (°) 90
b (Å) 12.773(2)	β (°) 90
c (Å) 37.264 (6)	γ (°) 90
Z 8	D_m (Mg m^{-3}) too air sensitive
V (Å^3) 5667 (2)	D_x (Mg m^{-3}) 1.255
Radiation MoKα	No. of reflections for lattice parameters 24
Wavelength (Å) 0.71073	θ range for lattice parameters (°) 11 < θ < 13
Absorption coefficient (mm^{-1}) 60.6	Temperature (K) 173
Crystal source Crystallization from hexane	
Crystal colour Orange	Crystal description needles
Crystal size (mm) 0.45 x 0.40 x 0.40	
DATA COLLECTION	
Diffractometer type CAD-4	Collection method ω/2θ
Absorption correction type (circle appropriate description) analytical integration (empirical) refdelf sphere cylinder none	Absorption correction (T_{min}, T_{max}) T_{min} = 99.65 T_{max} = 77.52
No. of reflections measured 4201	R_{int}
No. of independent reflections 3699	θ_{max}(°) 22.5
No. of observed reflections 2873	No. of standard reflections (and interval) 3, 1 hour
Criterion for observed $F^2 > 3\sigma(F^2)$	Variation of standards 10.3% linear decay
h_{min} 0	h_{max} 12
k_{min} 0	k_{max} 13
l_{min} 0	l_{max} 40

REFINEMENT

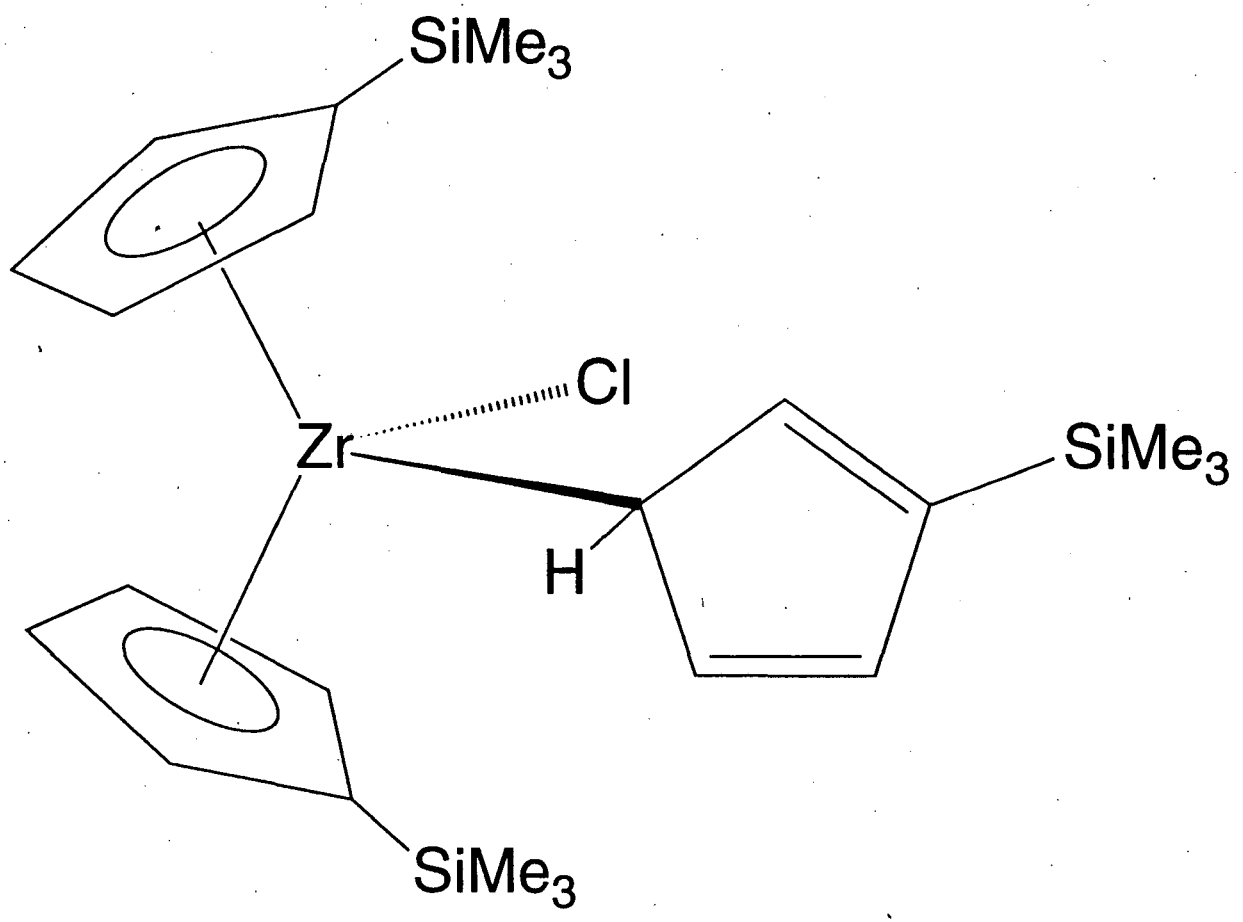
Treatment of hydrogen atoms (circle appropriate entry, or describe in box below) refall refxyz refU (noref)	F, F^2 or I F
R 0.0467	No. of parameters refined 290
wR 0.0585	No. of reflections used in refinement 2873
S 1.999	Weighting scheme $w=$ $1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max}$ 0	$(\Delta\rho)_{min}$ (e Å^{-3}) -0.39
Extinction correction method (if applied) Secondary	$(\Delta\rho)_{max}$ (e Å^{-3}) 1.81
Primary- and secondary-extinction values 5.1×10^{-8}	Source of atomic scattering factors International Tables

Please enter below, in grammatically correct text, details of any novel or unusual features of the experimental procedure; the method used to measure density, discussion of absolute structure and justification of unusually high R values or shift-to-e.s.d. values >1.0 should be included (attach extra sheet if necessary)

A chemical structural diagram should be attached to this form.

The remainder of the manuscript should consist of (i) double-spaced typed text and tables set out under the standard subheadings of §3 of the full Notes, (ii) figures and figure legends, (iii) supplementary data for deposition (see §4), (iv) signed Transfer of Copyright Agreement form, and (v) letter of submission.

Experimental. The title compound was prepared from $K(Me_3SiC_5H_4)$ and $ZrCl_4 \bullet 2THF$ in tetrahydrofuran followed by sublimation then crystallization from hexane as orange needles. An air sensitive crystal was mounted on the end of a 0.40 mm quartz capillary tube with a drop of Paratone N oil. Structure partially solved by direct methods (SHELXS86, Sheldrick, 1985), remaining atoms located by Fourier methods. Carbon atoms of the trimethylsilyl group on the η^1-cyclopentadienyl ring (C22, C23, and C24) had large thermal parameters and excess electron density existed between the carbon atoms indicating disorder of the trimethylsilyl group, disorder modeled by two sets of carbon atoms labelled (C22', C23', and C24') of occupancy 1/2 rotated by 180 ° about the Si3 - C11 axis. Residual electron density in the final Fourier synthesis is associated with this trimethylsilyl group. All non-hydrogen atoms refined with anisotropic thermal parameters in calculated positions with fixed thermal parameters 1.3 times that of the carbon to which they are attached. Atomic f for Zr, Cl, Si, C and H from *International Tables* (1974); structure refinement using MOLEN and local unpublished programs.


SiMe3
Cl
Zr
SiMe3
H
SiMe3

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