O(3)—Si(1)—O(5)	116.38 (10)	Si(1)—O(3)—C(3)	116.26 (18)
O(4)—Si(1)—O(5)	97.41 (10)	Si(1)—O(4)—C(4)	113.35 (17)
O(1)—Na(1)—O(1^{i})	87.62 (7)	Si(1)—O(5)—C(5)	127.05 (17)
O(1)—Na(1)—O(2^{ii})	109.58 (7)	O(1)—C(1)—C(2)	105.7 (2)
O(1)—Na(1)—O(3^{i})	104.86 (8)	O(2)—C(2)—C(1)	106.3 (2)
O(1)—Na(1)—O(5)	60.15 (7)	O(3)—C(3)—C(4)	106.5 (3)
O(1)—Na(1)—O(6)	129.00 (8)	O(4)—C(4)—C(3)	105.9 (3)
O(1^{i})—Na(1)—O(2^{ii})	145.82 (7)	O(5)—C(5)—C(6)	107.7 (2)
O(1^{i})—Na(1)—O(3)	59.68 (6)	O(6)—C(6)—C(5)	109.9 (3)
O(1^{i})—Na(1)—O(5)	108.27 (7)	N(1)—C(7)—C(8)	180.0
O(1^{i})—Na(1)—O(6)	98.40 (7)		

O(1)—Si(1)—O(2)—C(2)	9.2 (1)
O(4)—Si(1)—O(2)—C(2)	−176.8 (2)
O(1)—Si(1)—O(3)—C(3)	171.5 (2)
O(4)—Si(1)—O(3)—C(3)	−3.4 (2)
O(1)—Si(1)—O(4)—C(4)	−70.7 (2)
O(3)—Si(1)—O(4)—C(4)	−16.7 (1)
Si(1)—O(1)—C(1)—C(2)	−30.9 (11)
Si(1)—O(2)—C(2)—C(1)	−27.8 (11)
Si(1)—O(3)—C(3)—C(4)	20.7 (1)
Si(1)—O(4)—C(4)—C(3)	30.4 (2)
Si(1)—O(5)—C(5)—C(6)	−176.7 (3)
O(1)—C(1)—C(2)—O(2)	36.1 (1)
O(3)—C(3)—C(4)—O(4)	−30.8 (1)
O(5)—C(5)—C(6)—O(6)	57.4 (2)
O(2)—Si(1)—O(1)—C(1)	13.8 (2)
O(3)—Si(1)—O(1)—C(1)	−114.3 (2)
O(4)—Si(1)—O(1)—C(1)	−60.3 (2)
O(5)—Si(1)—O(1)—C(1)	129.2 (2)
O(3)—Si(1)—O(2)—C(2)	96.2 (2)
O(5)—Si(1)—O(2)—C(2)	−79.4 (2)
O(2)—Si(1)—O(3)—C(3)	83.5 (2)
O(5)—Si(1)—O(3)—C(3)	−101.0 (2)
O(2)—Si(1)—O(4)—C(4)	−144.9 (2)
O(5)—Si(1)—O(4)—C(4)	99.7 (2)
O(1)—Si(1)—O(5)—C(5)	158.5 (2)
O(2)—Si(1)—O(5)—C(5)	−112.3 (2)
O(3)—Si(1)—O(5)—C(5)	71.6 (2)
O(4)—Si(1)—O(5)—C(5)	−20.5 (1)

Symmetry codes: (i) $2 - x, -y, -z$; (ii) $1 + y, \frac{1}{2} - x, z$.

The crystal selected was mounted rapidly under a cold nitrogen stream on the diffractometer. Data were collected with a fixed background time and a scan speed of 5.0° min^{-1}. The crystal decomposed by reaction with atmospheric moisture within minutes of its removal from the cold nitrogen stream.

The structure was solved by direct methods (Sheldrick, 1990) and successive difference Fourier syntheses. Refinement was by a full-matrix least-squares method (Gabe *et al.*, 1992). All H atoms were refined with isotropic displacement parameters. The H atoms on the acetonitrile solvate were not located. No features of significance were noted in the final difference map.

Figures were produced by the *NRCVAX* version (Gabe *et al.*, 1992) of *ORTEP*II (Johnson, 1971).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and mean-plane data have been deposited with the IUCr (Reference: OH1063). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Chlorotris(trimethylsilylcyclopentadienyl)zirconium

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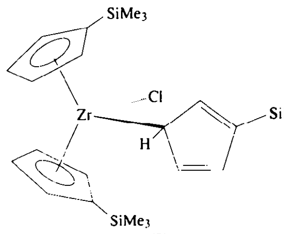
Abstract

The title compound, $[ZrCl(C_8H_{13}Si)_3]$, is a bent metallocene with two η^5-cyclopentadienyl ligands and one η^1-cyclopentadienyl ligand, *i.e.* chloro(3-trimethylsilylcyclopentadienyl-κC^1)bis(η^5-trimethylsilylcyclopentadienyl)zirconium. 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 (I) was synthesized as part of a study of zirconium compounds having several cyclopentadienyl rings. Zirconium compounds are known to possess up to three η^5-cyclopentadienyl rings as seen in the crystal structures of tetrakis(cyclopentadienyl)zirconium (Rogers, Vann Bynum & Atwood, 1978) and tris(cyclopentadienyl)zirconium triethylaluminium hydride (Kopf, Vollmer & Kaminsky, 1980); tris(cyclopentadienyl)zirconium chloride is also reported to possess three η^5-cyclopentadienyl rings (Strittmatter & Bursten, 1991). The *ansa*-bridged tris(cyclopentadienyl)zirconium and tris(cyclopentadienyl)hafnium chlorides also possess three η^5-cyclopentadienyl ligands (Diamond, Green, Popham & Chernega, 1993). However, the analogous tris(methylcyclopentadienyl)zirconium chloride (Etievant, Gautheron & Tainturier, 1977) is reported to possess one η^1- and two η^5-cyclopentadienyl rings. The ^{1}H NMR spectrum of the title compound revealed only one environment for the trimethylsilyl groups implying that the compound possesses either three η^5 ligands or that it is fluxional, with one η^1 and two η^5 ligands which interconvert rapidly on the NMR time scale. To determine which coordination geometry was correct the crystal structure of [ZrCl($Me_3SiC_5H_4$)$_3$], (I), was determined.



(I)

An *ORTEP* (Johnson, 1965) drawing of the title complex is shown in Fig. 1. The Zr—C distances in the η^5-cyclopentadienyl rings vary from 2.488 (6) Å for Zr—C3 to 2.591 (5) Å for Zr—C1. While the range of bond distances is larger than that of [ZrR_2(η^5-C_5H_5)$_2$] compounds (Rogers, Vann Bynum & Atwood, 1978, and references therein), it is similar to that found in [Zr(η^5-C_5H_5)$_3$(η^1-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 those of the η^1-cyclopentadienyl ring of [Ti(η^5-C_5H_5)$_2$(η^1-C_5H_5)$_2$] (Calderon, Cotton, DeBoer & Takats, 1971). The Zr—C14 distance is similar to the Zr—C(η^1) distance found in [Zr(η^5-C_5H_5)$_3$(η^1-C_5H_5)] [2.776(6) Å].

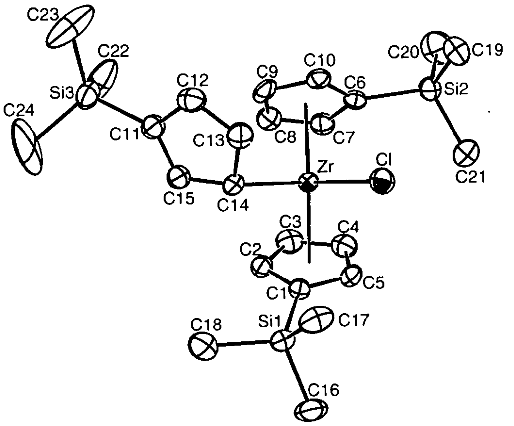


Fig. 1. A view (*ORTEP*; Johnson, 1965) of the [ZrCl($C_5H_4SiMe_3$)$_3$] molecule showing 50% probability ellipsoids. H atoms are omitted and only one set of the disordered C22–C24 methyl C atoms is displayed.

Experimental

The title compound was prepared from K($Me_3SiC_5H_4$) and $ZrCl_4.2C_4H_8O$ in tetrahydrofuran followed by sublimation and subsequent 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.

Crystal data

[ZrCl($C_8H_{13}Si$)$_3$]
M_r = 538.51
Orthorhombic
Pbca
a = 11.979 (2) Å
b = 12.773 (2) Å
c = 37.264 (6) Å
V = 5702 (2) Å^3
Z = 8
D_x = 1.255 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 24 reflections
θ = 11–13°
μ = 0.61 mm^{-1}
T = 173 K
Needles
0.45 × 0.40 × 0.40 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
T_{min} = 0.775, T_{max} = 0.997
4201 measured reflections
3699 independent reflections
2873 observed reflections [$F^2 > 3\sigma(F^2)$]

θ_{max} = 22.5°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 40$
3 standard reflections
frequency: 60 min
intensity variation: 10.3% (linear decay)

Refinement

Refinement on F
R = 0.0467
wR = 0.0585
S = 1.999
2873 reflections
290 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} < 0.01$

$\Delta\rho_{max}$ = 1.81 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}
Extinction correction: secondary (Stout & Jensen, 1968)
Extinction coefficient: 5.1 × 10^{-8}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
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 (4)	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 geometric parameters* (Å, °)

*Cp*1 and *Cp*2 are the centroids of the η^5-cyclopentadienyl rings.

Zr—Cl	2.442 (1)	Zr—C14	2.396 (5)
Zr—*Cp*1	2.227	Zr—*Cp*2	2.200
Zr—C1	2.591 (5)	Zr—C6	2.536 (5)
Zr—C2	2.519 (5)	Zr—C7	2.501 (5)
Zr—C3	2.488 (6)	Zr—C8	2.500 (5)
Zr—C4	2.491 (6)	Zr—C9	2.500 (5)
Zr—C5	2.553 (5)	Zr—C10	2.509 (5)
C11—C12	1.447 (8)	C11—C15	1.381 (8)
C12—C13	1.383 (8)	C13—C14	1.447 (8)
C14—C15	1.446 (8)		
*Cp*1—Zr—*Cp*2	127.8	Cl—Zr—C14	92.1 (1)

The structure was solved partially by direct methods (*SHELXS*86; Sheldrick, 1985), the remaining atoms being located by Fourier methods. C atoms of the trimethylsilyl group on the η^1-cyclopentadienyl ring (C22, C23 and C24) had large displacement parameters and excess electron density between them indicating disorder which was modeled by two sets of methyl C atoms (occupancy 0.5) related by a rotation of 180° about the Si3—C11 axis. Residual electron density in the final Fourier synthesis is associated with this trimethylsilyl group. All non-H atoms were refined with anisotropic displacement parameters. Each H atom was placed in a calculated position with a fixed displacement parameter of 1.3 times that of the C atom to which it is attached. The structure refinement used *MolEN* (Fair, 1990) and local unpublished programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: MU1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Oxobis(2,4-pentanedionato)vanadium(IV), a Redetermination

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Abstract

A redetermination of oxobis(2,4-pentanedionato)vanadium(IV), [VO($C_5H_7O_2$)$_2$], has been undertaken using high-resolution Mo data. Geometrical parameters do not differ significantly from those reported earlier [Dodge, Templeton & Zalkin (1961). *J. Chem. Phys.* **35**, 55–67; Hon, Belford & Pfluger (1965). *J. Chem. Phys.* **43**, 3111–3115], but the standard deviations are improved by an order of magnitude. Important structural parameters: V—O(basal) 1.967 (1)–1.970 (1) Å and V═O(apical) 1.584 (2) Å.

Comment

Current interest in orally active insulin mimics, particularly vanadium compounds (Shechter, 1990; Shechter *et al.*, 1990), has prompted a redetermination of the structure of oxobis(2,4-pentanedionato)vanadium(IV), (I). Since some of the promising vanadium-containing insulin mimics are structurally related to vanadyl bis(β-