Acta Crystallographica Section E
Structure Reports Online

ISSN 1600-5368

Bis[η^5-1,3-bis(trimethylsilyl)cyclopentadienyl]vanadium(II)

Chadwick D. Sofield, Marc D. Walter* and Richard A. Andersen

Chemical Sciences Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, CA 94720, USA

Correspondence e-mail: mwalter@rhrk.uni-kl.de

Key indicators

Single-crystal X-ray study
T = 137 K
Mean σ(C–C) = 0.005 Å
R factor = 0.048
wR factor = 0.134
Data-to-parameter ratio = 18.9

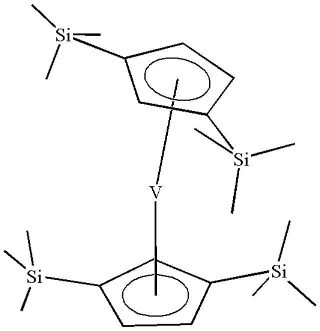
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 11 August 2004
Accepted 16 August 2004
Online 21 August 2004

The title compound, [V($C_{11}H_{21}Si_2$)$_2$], crystallizes in space group $C2/c$ with the V atom located on a twofold symmetry axis. The vanadium(II) center is coordinated by two 1,3-bis(trimethylsilyl)cyclopentadienyl rings (Cp″) to form a slightly bent metallocene [Cp(centroid)—V—Cp(centroid) = 173.0 (1)°].

Comment

Although the chemistry of vanadocenes is extensively discussed in the literature, crystal structures of base-free vanadocenes are still quite rare. The crystal structures of Cp_2V (Weiss & Fischer, 1955; Antipin & Boese, 1996; Rogers *et al.*, 1981), (C_5Me_5)$_2$V (Gambrotta *et al.*, 1984), (C_5HPh_4)$_2$V (Castellani *et al.*, 1987), (^{t}BuC_5H_4)$_2$V (Derraz *et al.*, 1995) and (1,2,4-^{i}Pr$_3C_5H_2$)$_2$V (Overby *et al.*, 1999) have been reported.



(I)

Bis[η^5-1,3-bis(trimethylsilyl)cyclopentadienyl]vanadium(II), (Cp″$_2$V) (I) (Fig. 1), crystallizes in space group $C2/c$. The V atom occupies a special position with twofold symmetry and the complete complex is generated from one V and one Cp″ unit. Table 1 lists selected bond lengths and angles. ‘Interlocking’ of the four sterically demanding trimethylsilyl groups results in a nearly eclipsed conformation of the essentially planar five-membered rings with a slight tilt [Cp(centroid)—V—Cp(centroid) = 173.0(1)°]. The averaged V—C(ring) distance of 2.267 (1) Å is comparable to that in vanadocene and its derivatives [Cp_2V: 2.269 (6) Å (Antipin & Boese, 1996); (C_5HPh_4)$_2$V: 2.268 (4) Å (Castellani *et al.*, 1987); (1,2,4-^{i}Pr$_3C_5H_2$)$_2$V: 2.274 (8) Å (Overby *et al.*, 1999); (^{t}BuC_5H_4)$_2$V: 2.274 (1) Å (Derraz *et al.*, 1995)], as are the C—C bond lengths [average 1.420 (2) Å] within the cyclopentadienyl ring. One of the trimethylsilyl groups for each Cp″ is slightly bent out of the plane of the cyclopentadienyl ring to which they are bonded [the angle between the Si—C(Cp) and the plane of the Cp ring for Si2 is 3.58 (16)°]. Cp″$_2$V is

DOI: 10.1107/S1600536804020276

isomorphous with its Fe analogue (Okuda & Herdtweck, 1989).

Experimental

Blue crystals of $[(C_5H_3(SiMe_3)_2)_2V]$ were obtained in 40% yield from the reaction of $[(C_5H_3(SiMe_3)_2)_2VCl]$ (11.86 g, 23.5 mmol) with K/Hg (20 ml Hg and 4.6 g K) in *n*-hexane at room temperature, followed by filtration and slow cooling to 253 K of a concentrated solution. Calculated for $C_{22}H_{42}Si_4V$: C 56.24, H 9.01%; found: C 56.60, H 8.85%. ^{1}H NMR (C_6D_6, 90 MHz): 4.08 p.p.m. (*br s*, $\nu_{1/2}$ = 93.6 Hz). IR (Nujol): 3065 (*w*), 1400 (*w*), 1372 (*s*), 1320 (*w*), 1200 (*s*), 923 (*sh*), 910 (*s*), 882 (*s*), 730 (*vw*), 690 (*m*), 628 (*s*), 488 (*m*), 425 (*m*), 410 (*vw*), 380 (*m*), 370 (*m*), 280 (*vw*), 260 (*m*), 240 (*w*) cm^{-1}. The crystal (m.p. 426 K) was handled under a nitrogen atmosphere, mounted on a glass fiber with Paratone-N oil and cooled to 137 (2) K for data collection.

Crystal data

$[V(C_{11}H_{21}Si_2)_2]$
$M_r = 469.86$
Monoclinic, $C2/c$
$a = 12.451\ (4)$ Å
$b = 18.447\ (6)$ Å
$c = 12.676\ (5)$ Å
$\beta = 99.720\ (8)^\circ$
$V = 2869.8\ (17)$ Å^3
$Z = 4$

$D_x = 1.087$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2367 reflections
$\theta = 2$–25°
$\mu = 0.52$ mm^{-1}
$T = 137\ (2)$ K
Block, blue
0.34 × 0.30 × 0.10 mm

Data collection

Bruker SMART 1K CCD diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\rm min} = 0.874$, $T_{\rm max} = 0.946$
6382 measured reflections

2432 independent reflections
1690 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\rm max} = 25.5^\circ$
$h = -14 \rightarrow 13$
$k = -21 \rightarrow 21$
$l = -5 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.134$
$S = 1.02$
2432 reflections
129 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0818P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.97$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

V1—C1	2.261 (3)	V1—C4	2.268 (3)
V1—C2	2.255 (3)	V1—C5	2.254 (3)
V1—C3	2.293 (3)	V1—*Cg*1	1.92 (1)
*Cg*1—V1—*Cg*1$^{\rm i}$	173.0 (1)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$. Note: *Cg*1 is the centroid of the cyclopentadienyl ring.

Methyl H atoms were added at calculated positions using a riding model, with C—H distances of 0.98 Å and $U_{\rm iso}$(H) = 1.5 $U_{\rm eq}$(C). For each methyl group, the torsion angle which defines the orientation about the C—C bond was refined. The remaining methyne H atoms were included in the model at calculated positions using the riding model, with C—H distances of 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 1995–1999); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

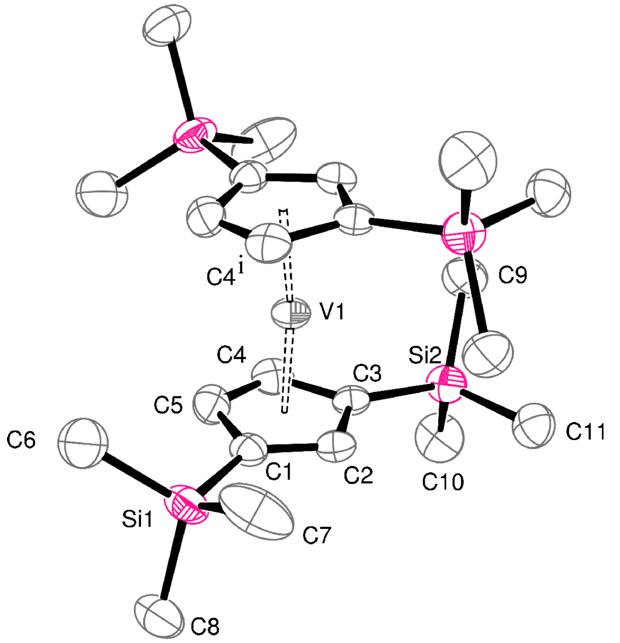


Figure 1
View of the structure of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy, under contract No. DE-AC03-76SF00098. We thank Dr Fred Hollander (at CHEXRAY, the UC Berkeley X-ray Diffraction Facility) for assistance with the crystallography, and the state Rhineland Palatinate (Germany) for a graduate grant (MDW).

References

Antipin, M. Yu. & Boese, R. (1996). *Acta Cryst.* B**52**, 314–322.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruker (1995–1999). *SMART*. Version 5.0.54d. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2002). *SAINT*. Version 6.40. Bruker AXS Inc., Madison, Wisconsin, USA.
Castellani, M. P., Geib, S. J., Rheingold, A. L. & Trogler, W. C. (1987). *Organometallics*, **6**, 1703–1712.
Derraz, Y., Cyr-Athis, O., Choukroun, O., Valade, L., Cassoux, P., Dahan, F. & Teyssandier, F. (1995). *J. Mater. Chem.* **5**, 1775–1778.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Gambrotta, S., Floriani, C., Chiesi-Villa, A. & Guastini, C. (1984). *Inorg. Chem.* **23**, 1739–1747.
Okuda, J. & Herdtweck, E. (1989). *J. Organomet. Chem.* **373**, 99–105.
Overby, J. S., Jayaratne, K. C., Schoell, N. J. & Hanusa, T. P. (1999). *Organometallics*, **18**, 1663–1668.
Rogers, R. D., Atwood, J. L., Foust, D. & Rausch, M. D. (1981). *J. Cryst. Mol. Struct.* **11**, 183–188.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen. Germany.
Weiss, E. & Fischer, E. O. (1955). *Z. Allg. Anorg. Chem.* **278**, 219–224.