= 1.0, and $w_s(\sin\theta < 0.543) = (\sin\theta/0.543)^{2.5}$ and $w_s(\sin\theta \geq 0.543) = 1.0$.

Data collection and cell refinement were carried out using *CAD*-4 *Software* (Enraf-Nonius, 1989). The *Xtal*3.0 system (Hall & Stewart, 1990) was used for correlation and reduction of data, structure refinement and interpretation. Calculations were performed on VAX 8550 computers at the University Computer Centre, Ljubljana. *ORTEP*II (Johnson, 1976) was used for molecular graphics.

We wish to thank Professor Ljubo Golič for much useful advice during this structure determination, and also the Ministry of Science and Technology of the Republic of Slovenia for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1142). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Nine-Membered Metallacyclic Metalloxycarbene Vanadium Complex

Matthias Grehl, Martin Berlekamp and
Gerhard Erker

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

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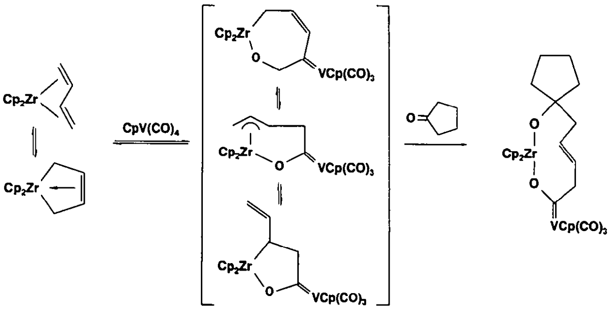
Abstract

The title compound, tricarbonyl-2κ^3C-tris[1,1,2(η^5)-cyclopentadienyl][μ-1-hydroxy-5-(1-hydroxycyclopentyl)-pent-3-en-1-ylidene(4−)-1κ^2O,O':2κC^1]vanadiumzirconium–toluene (1/0.5), $[\{Zr(C_5H_5)_2\}(\mu\text{-}C_{10}H_{14}O_2)\text{-}\{V(CO)_3(C_5H_5)\}].0.5C_7H_8$, is a carbene complex of the *d*-block elements and has an important role in organometallic chemistry. Only a few carbene–vanadium complexes have been characterized by X-ray diffraction so far. X-ray structure analysis showed that the central nine-membered metallacyclic framework contains a *trans*-configured C═C double bond between C(6) and C(7).

Comment

Carbene complexes of *d*-block elements are finding increasing application in stoichiometric organic synthesis and catalysis (Casey & Alper, 1976; Brown, 1980; Dötz, 1984; Dötz *et al.*, 1983). The new carbene synthesis described by Berlekamp & Erker (1993) makes use of the high reactivity of alkene–metallocene complexes and the high tendency of the Group IV elements to form thermodynamically favourable *M*—O bonds. Thus, (butadiene)ZrCp$_2$ (Cp = cyclopentadienyl) complexes react with metal carbonyls such as CpV(CO)$_4$ as shown in the scheme below. Subsequent addition of cyclopentanone converts the intermediate complex into the nine-membered metallacyclic metalloxycarbene vanadium complex (3), the structure of which is described here.



cis-/trans-(1) (2) (3)

(I)

The title complex is isostructural with the corresponding hafnium metalloxycarbene vanadium complex, the X-ray structure of which was determined previously as it shows greater thermodynamic stability. The central nine-membered metallacyclic framework of the zirconocene complex contains a *trans*-configured C═C double bond between C(6) and C(7) [1.312 (3) Å]. The adjacent C(5)—C(6) [1.493 (3) Å] and C(7)—C(8) [1.488 (3) Å] bond lengths are characteristic of C_{sp^2}—C_{sp^3} single-bond distances (Berlekamp & Erker, 1993; Allen *et al.*, 1987). These distances are equal, to within one e.s.d., to the bond lengths found in the corresponding hafnium complex. This arrangement of the *trans*-C═C bond inside the rigid nine-membered metallacycle means that the complex is chiral (Berlekamp & Erker, 1993). The Zr—O bonds are rather short at 2.084 (2) Å

[Zr(1)—O(4)] and 1.908 (2) Å [Zr(1)—O(5)] but comparable with the distances found in the hafnium complex [2.066 (3) and 1.900 (3) Å]. The O atoms coordinated to Zr approach a linear arrangement [C(4)—O(4)—Zr(1) 168.2 (2) and C(9)—O(5)—Zr(1) 172.3 (2)°] with *sp*-hybridized O atoms. The angles between the planes of the Cp rings at the Zr atom and the plane formed by the atoms C(4), O(4), Zr(1), O(5) and C(9) are 28.1 and 26.6°, respectively. The C(6)═C(7) π bond is oriented directly in front of the Zr atom, as in the corresponding Hf complex, but the separation between the metal atom and the π bond is in both cases clearly outside the range of any bonding interaction. The environment about C(4) of the carbene ligand is trigonal planar [O(4)—C(4)—V(1) 126.9 (2), C(5)—C(4)—V(1) 120.1 (2), O(4)—C(4)—C(5) 112.9 (2)°] and the bond length C(4)—C(5) is 1.540 (3) Å [1.546 (7) Å in the corresponding Hf complex], which is at the outer limit for a C_{sp^2}—C_{sp^3} bond. The C(4)—V(1) distance of 2.096 (2) Å is similar to the distance found in the Hf complex. The C(4)—O(4) distance is rather short [1.280 (2) Å] but in a range typical for C═O double bonds. A similar distance [1.282 (6) Å] found in the corresponding Hf complex is representative of all these metalloxycarbene vanadium complexes.

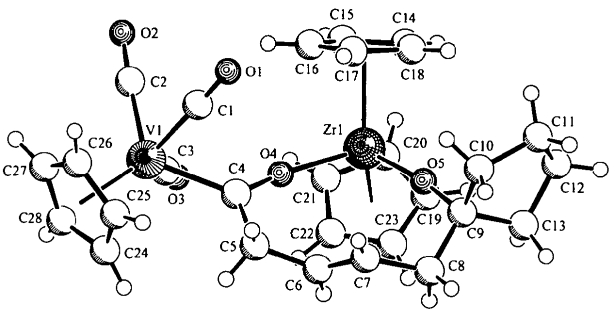


Fig. 1. A *SCHAKAL*92 (Keller, 1992) plot of the metalloxycarbene complex with the atomic numbering scheme.

Experimental

Crystal data

$[VZr(C_{10}H_{14}O_2)(C_5H_5)_3(CO)_3].0.5C_7H_8$
$M_r = 633.74$
Monoclinic
$P2_1/n$
$a = 8.311\ (1)$ Å
$b = 17.111\ (1)$ Å
$c = 20.500\ (2)$ Å
$\beta = 101.44\ (1)°$
$V = 2857.3\ (4)$ Å^3
$Z = 4$
$D_x = 1.473$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.90$–$20.82°$
$\mu = 0.73$ mm^{-1}
$T = 293$ K
Irregular
$0.53 \times 0.48 \times 0.31$ mm
Dark violet

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan
$T_{\min} = 0.88$, $T_{\max} = 0.99$
8762 measured reflections
8281 independent reflections
6364 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.014$
$\theta_{\max} = 30.42°$
$h = 0 \rightarrow 11$
$k = -24 \rightarrow 0$
$l = -29 \rightarrow 28$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.061$
$wR(F^2) = 0.091$
$S = 1.268$
8065 reflections
368 parameters
H atoms placed in calculated positions

Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}
Extinction correction: none
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)

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

	x	y	z	$U_{\rm eq}$
Zr(1)	0.3140 (1)	0.3359 (1)	0.2375 (1)	0.032 (1)
V(1)	0.4971 (1)	0.2086 (1)	0.0440 (1)	0.034 (1)
O(1)	0.7277 (2)	0.1886 (1)	0.1786 (1)	0.057 (1)
O(2)	0.4101 (3)	0.0488 (1)	0.0944 (1)	0.068 (1)
O(3)	0.1290 (3)	0.2202 (2)	0.0455 (1)	0.075 (1)
O(4)	0.4003 (2)	0.3115 (1)	0.1510 (1)	0.038 (1)
O(5)	0.4419 (2)	0.4231 (1)	0.2758 (1)	0.040 (1)
C(1)	0.6386 (3)	0.1964 (1)	0.1281 (1)	0.040 (1)
C(2)	0.4418 (3)	0.1085 (2)	0.0739 (1)	0.045 (1)
C(3)	0.2663 (3)	0.2160 (2)	0.0450 (1)	0.047 (1)
C(4)	0.4754 (3)	0.3073 (1)	0.1023 (1)	0.033 (1)
C(5)	0.5658 (3)	0.3834 (1)	0.0917 (1)	0.044 (1)
C(6)	0.5239 (3)	0.4502 (1)	0.1321 (1)	0.041 (1)
C(7)	0.6198 (3)	0.4789 (2)	0.1853 (1)	0.042 (1)
C(8)	0.5615 (3)	0.5336 (1)	0.2321 (1)	0.045 (1)
C(9)	0.5354 (3)	0.4913 (1)	0.2952 (1)	0.037 (1)
C(10)	0.6959 (3)	0.4684 (2)	0.3428 (2)	0.053 (1)
C(11)	0.6610 (4)	0.4727 (2)	0.4132 (2)	0.065 (1)
C(12)	0.4839 (4)	0.5012 (2)	0.4064 (1)	0.057 (1)
C(13)	0.4479 (3)	0.5417 (2)	0.3389 (1)	0.046 (1)
C(14)	0.3016 (4)	0.2508 (2)	0.3357 (2)	0.060 (1)
C(15)	0.2687 (4)	0.2004 (2)	0.2806 (2)	0.059 (1)
C(16)	0.4116 (4)	0.1934 (2)	0.2549 (2)	0.055 (1)
C(17)	0.5329 (4)	0.2398 (2)	0.2941 (2)	0.054 (1)
C(18)	0.4657 (4)	0.2734 (2)	0.3447 (1)	0.057 (1)
C(19)	0.0645 (4)	0.4107 (2)	0.2538 (2)	0.067 (1)
C(20)	0.0109 (3)	0.3343 (2)	0.2392 (2)	0.063 (1)
C(21)	0.0228 (3)	0.3184 (2)	0.1735 (2)	0.060 (1)
C(22)	0.0799 (3)	0.3858 (2)	0.1474 (2)	0.060 (1)
C(23)	0.1047 (4)	0.4428 (2)	0.1962 (2)	0.065 (1)
C(24)	0.5333 (4)	0.2808 (2)	−0.0456 (1)	0.050 (1)
C(25)	0.6875 (3)	0.2607 (2)	−0.0086 (1)	0.048 (1)
C(26)	0.7030 (4)	0.1792 (2)	−0.0111 (2)	0.053 (1)
C(27)	0.5587 (4)	0.1491 (2)	−0.0492 (2)	0.058 (1)
C(28)	0.4532 (4)	0.2111 (2)	−0.0703 (1)	0.057 (1)
C(29)	−0.0432 (10)	0.5330 (4)	0.0251 (4)	0.069 (2)
C(30)	−0.1445 (8)	0.4770 (5)	−0.0112 (4)	0.072 (3)
C(31)	−0.0804 (15)	0.4241 (4)	−0.0507 (3)	0.098 (4)
C(32)	0.0849 (17)	0.4271 (5)	−0.0540 (4)	0.138 (11)
C(33)	0.1862 (10)	0.4831 (6)	−0.0177 (5)	0.097 (3)
C(34)	0.1222 (9)	0.5361 (4)	0.0219 (4)	0.072 (3)
C(35)	−0.1072 (22)	0.5869 (12)	0.0653 (10)	0.119 (7)

Table 2. *Selected geometric parameters* (Å, °)

Zr(1)—O(5)	1.908 (2)	Zr(1)—O(4)	2.084 (2)
Zr(1)—C(14)	2.503 (3)	Zr(1)—C(19)	2.514 (3)
Zr(1)—C(20)	2.526 (3)	Zr(1)—C(21)	2.531 (3)
Zr(1)—C(15)	2.536 (3)	Zr(1)—C(18)	2.542 (3)
Zr(1)—C(22)	2.549 (3)	Zr(1)—C(23)	2.550 (3)
Zr(1)—C(17)	2.555 (3)	Zr(1)—C(16)	2.572 (3)
V(1)—C(1)	1.896 (3)	V(1)—C(2)	1.906 (3)
V(1)—C(3)	1.926 (3)	V(1)—C(4)	2.096 (2)
V(1)—C(25)	2.266 (2)	V(1)—C(24)	2.282 (3)
V(1)—C(26)	2.285 (3)	V(1)—C(28)	2.300 (3)
V(1)—C(27)	2.311 (3)	O(1)—C(1)	1.154 (3)
O(2)—C(2)	1.154 (3)	O(3)—C(3)	1.145 (3)
O(4)—C(4)	1.280 (2)	O(5)—C(9)	1.415 (3)
C(4)—C(5)	1.540 (3)	C(5)—C(6)	1.493 (3)
C(6)—C(7)	1.312 (3)	C(7)—C(8)	1.488 (3)
C(8)—C(9)	1.536 (4)	C(9)—C(13)	1.527 (3)
C(9)—C(10)	1.539 (3)	C(10)—C(11)	1.528 (4)
C(11)—C(12)	1.530 (4)	C(12)—C(13)	1.523 (4)
C(14)—C(18)	1.394 (5)	C(14)—C(15)	1.404 (4)
C(15)—C(16)	1.396 (4)	C(16)—C(17)	1.404 (4)
C(17)—C(18)	1.395 (4)	C(19)—C(20)	1.393 (5)
C(19)—C(23)	1.402 (5)	C(20)—C(21)	1.398 (4)
C(21)—C(22)	1.393 (5)	C(22)—C(23)	1.383 (5)
C(24)—C(25)	1.396 (4)	C(24)—C(28)	1.410 (4)
C(25)—C(26)	1.402 (4)	C(26)—C(27)	1.394 (4)
C(27)—C(28)	1.390 (5)		
O(5)—Zr(1)—O(4)	104.41 (7)	C(1)—V(1)—C(2)	75.79 (11)
C(1)—V(1)—C(3)	115.93 (11)	C(2)—V(1)—C(3)	75.61 (12)
C(1)—V(1)—C(4)	71.24 (9)	C(2)—V(1)—C(4)	119.17 (10)
C(3)—V(1)—C(4)	75.12 (10)	C(4)—O(4)—Zr(1)	168.2 (2)
C(9)—O(5)—Zr(1)	172.3 (2)	O(1)—C(1)—V(1)	178.4 (2)
O(2)—C(2)—V(1)	177.5 (3)	O(3)—C(3)—V(1)	179.8 (3)
O(4)—C(4)—C(5)	112.9 (2)	O(4)—C(4)—V(1)	126.9 (2)
C(5)—C(4)—V(1)	120.1 (2)	C(6)—C(5)—C(4)	113.3 (2)
C(7)—C(6)—C(5)	125.3 (2)	C(6)—C(7)—C(8)	123.3 (2)
C(7)—C(8)—C(9)	111.4 (2)	O(5)—C(9)—C(13)	109.4 (2)
O(5)—C(9)—C(8)	108.2 (2)	C(13)—C(9)—C(8)	113.1 (2)
O(5)—C(9)—C(10)	109.1 (2)	C(13)—C(9)—C(10)	103.0 (2)
C(8)—C(9)—C(10)	113.9 (2)	C(11)—C(10)—C(9)	106.5 (2)
C(10)—C(11)—C(12)	106.8 (2)	C(13)—C(12)—C(11)	103.9 (2)
C(12)—C(13)—C(9)	104.2 (2)	C(18)—C(14)—C(15)	107.9 (3)
C(16)—C(15)—C(14)	108.1 (3)	C(15)—C(16)—C(17)	107.7 (3)
C(18)—C(17)—C(16)	108.1 (3)	C(14)—C(18)—C(17)	108.2 (3)
C(20)—C(19)—C(23)	107.9 (3)	C(19)—C(20)—C(21)	108.0 (3)
C(22)—C(21)—C(20)	107.7 (3)	C(23)—C(22)—C(21)	108.6 (3)
C(23)—C(22)—Zr(1)	74.3 (2)	C(21)—C(22)—Zr(1)	73.4 (2)
C(22)—C(23)—C(19)	107.8 (3)	C(22)—C(23)—Zr(1)	74.2 (2)
C(19)—C(23)—Zr(1)	72.5 (2)	C(25)—C(24)—C(28)	107.7 (3)
C(25)—C(24)—V(1)	71.5 (2)	C(28)—C(24)—V(1)	72.8 (2)
C(24)—C(25)—C(26)	107.8 (3)	C(24)—C(25)—V(1)	72.7 (2)
C(26)—C(25)—V(1)	72.8 (2)	C(27)—C(26)—C(25)	108.3 (3)
C(27)—C(26)—V(1)	73.3 (2)	C(25)—C(26)—V(1)	71.3 (2)
C(28)—C(27)—C(26)	108.1 (3)	C(28)—C(27)—V(1)	72.0 (2)
C(26)—C(27)—V(1)	71.4 (2)	C(27)—C(28)—C(24)	108.1 (3)
C(27)—C(28)—V(1)	72.9 (2)	C(24)—C(28)—V(1)	71.4 (2)

In addition to the metalloxycarbene complex, a toluene molecule, disordered about a crystallographic centre of inversion, was located. The positions of the six C atoms of the phenyl ring were refined as a rigid body with an occupancy factor of 0.5 and the methyl C atom was located by a difference Fourier analysis.

Data collection and cell refinement: *EXPRESS* (Enraf–Nonius, 1993). Data reduction: local programs. Structure solution: *SHELXS*86 (Sheldrick, 1985). Structure refinement: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SCHAKAL*92 (Keller, 1992).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: JZ1002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrabutylbis[(*N*,*N*-diethylthiocarbamoylthio)acetato]distannoxane Dimer

SEIK WENG NG

Institute of Advanced Studies, University of Malaya,
59100 Kuala Lumpur, Malaysia

V. G. KUMAR DAS

Department of Chemistry, University of Malaya,
59100 Kuala Lumpur, Malaysia

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Abstract

In the centrosymmetric title compound, octabutyl-$1\kappa^2C,2\kappa^2C,3\kappa^2C,4\kappa^2C$-tetrakis[$\mu$-(*N*,*N*-diethylthiocarbamoylthio)acetato]-$1{:}2\kappa^2O,O';2{:}3\kappa^2O;3{:}4\kappa^2O,O'$;-$1{:}4\kappa^2O$-bis-$\mu_3$-oxo-$1{:}2{:}3\kappa^3O;1{:}3{:}4\kappa^3O$-tetratin, $[Sn_4O_2(C_7H_{12}NO_2S_2)_4(C_4H_9)_8]$, one Sn atom is five-coordinate having *cis*-C_2SnO_3 trigonal bipyramidal geometry, whereas the other is six-coordinate having C_2SnO_4 skew-trapezoidal bipyramidal geometry with apical disposition of the butyl groups.

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