C20	0.4123 (2)	0.7930 (2)	0.9116 (2)	0.0470 (6)
C21	0.4253 (3)	0.8458 (2)	0.8400 (2)	0.0615 (8)
C22	0.5404 (4)	0.8642 (3)	0.8085 (3)	0.0809 (11)
C23	0.6407 (4)	0.8292 (3)	0.8478 (3)	0.0891 (15)
C24	0.6329 (3)	0.7747 (3)	0.9192 (3)	0.0734 (10)
C25	0.5179 (3)	0.7565 (2)	0.9515 (2)	0.0542 (7)
C26	0.6015 (4)	0.6647 (3)	1.0632 (3)	0.0822 (12)

Table 3. *Selected distances (Å) and angles (°) in complexes (1) and (2)*

	(1) *M* = Cr	(2) *M* = Mo
M—P	2.4568 (5)	2.5883 (7)
M—C1	1.880 (2)	2.015 (3)
M—C2	1.898 (2)	2.037 (4)
M—C3	1.899 (2)	2.055 (3)
M—C4	1.890 (2)	2.040 (3)
M—C5	1.851 (2)	1.981 (3)
P—C6	1.840 (2)	1.837 (3)
P—C13	1.836 (2)	1.839 (3)
P—C20	1.838 (2)	1.828 (3)
O1—C1	1.141 (3)	1.137 (3)
O2—C2	1.133 (3)	1.139 (4)
O3—C3	1.138 (2)	1.131 (4)
O4—C4	1.141 (3)	1.144 (4)
O5—C5	1.135 (3)	1.143 (4)
O1—C1—*M*	172.9 (2)	177.5 (3)
O2—C2—*M*	177.5 (2)	174.8 (3)
O3—C3—*M*	174.4 (2)	179.5 (3)
O4—C4—*M*	176.9 (2)	174.3 (3)
O5—C5—*M*	178.8 (2)	178.3 (3)
C1—*M*—P	94.47 (7)	89.85 (9)
C2—*M*—P	87.16 (6)	93.88 (9)
C3—*M*—P	93.61 (6)	88.92 (9)
C4—*M*—P	91.40 (6)	93.36 (9)
C5—*M*—P	178.25 (7)	178.19 (9)
C6—P—*M*	116.77 (6)	115.29 (9)
C13—P—*M*	108.23 (5)	119.78 (9)
C20—P—*M*	119.39 (5)	110.59 (9)
C13—P—C6	103.60 (7)	101.37 (12)
C20—P—C6	102.12 (7)	103.68 (13)
C13—P—C20	105.11 (7)	104.39 (12)

For both compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXTL/PC* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXL93*; geometrical calculations: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1238). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Dioxo(η^5-pentamethylcyclopentadienyl)(trimethylsilylmethyl)tungsten(VI)

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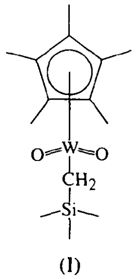
Abstract

(η^5-C_5Me_5)WO_2(CH_2SiMe_3), which has crystallographic mirror symmetry, exhibits the three-legged piano stool geometry typical for complexes of this type. The pentamethylcyclopentadienyl ligand is asymmetrically bound to the metal atom [W—C = 2.321 (8)–2.477 (4) Å]. The W=O and W—C(alkyl) distances are 1.717 (4) and 2.128 (8) Å, respectively.

Comment

The physical properties of (η^5-C_5Me_5)WO_2(CH_2SiMe_3), (I), have been reported elsewhere (Legzdins, Rettig & Sayers, 1994). Further examples of related organometallic oxo chemistry are fully described in the literature (Legzdins, Phillips & Sanchez, 1989; Legzdins, Rettig & Sanchez, 1985). The structure of (η^5-C_5Me_5)WO_2(CH_2SiMe_3) is very similar to that of the cyclopentadienyl derivative (η^5-C_5H_5)WO_2(CH_2SiMe_3) (Legzdins, Rettig & Sanchez, 1985). Corresponding



(I)

bond lengths and angles involving the metal atom in the two derivatives are equal within the limits of experimental error and are as expected. Unlike the present molecule, the η^5-C_5H_5 derivative does not exhibit crystallographic mirror symmetry, although the molecule has an approximate mirror plane. All intermolecular contacts correspond to normal van der Waals interactions, the shortest intermolecular contact between non-H atoms being O(1)···C(4) [3.430 (9) Å].

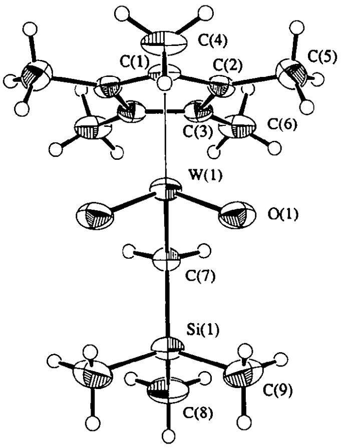


Fig. 1. Perspective view of the (η^5-C_5Me_5)$WO_2(CH_2SiMe_3)$ molecule (33% probability ellipsoids are shown for the non-H atoms).

Experimental

The complex was synthesized by reaction of an excess of H_2O with a solution of $[(\eta^5\text{-}C_5Me_5)W(NO)(CH_2SiMe_3)(NCMe)_2]$-$BF_4$ in CH_3CN, as described previously (Legzdins, Rettig & Sayers, 1994).

Crystal data

$[WO_2(C_{10}H_{15})(C_4H_{11}Si)]$
$M_r = 438.29$
Orthorhombic
Pnma
$a = 9.450 (2)$ Å
$b = 12.383 (3)$ Å
$c = 14.453 (2)$ Å
$V = 1691.4 (4)$ Å^3
$Z = 4$
$D_x = 1.721$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 13.2$–$15.7°$
$\mu = 6.90$ mm^{-1}
$T = 294.2$ K
Irregular
0.50 × 0.35 × 0.20 mm
Yellow

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.423$, $T_{max} = 1.000$
2242 measured reflections
2242 independent reflections

1202 observed reflections $[I > 3\sigma(I)]$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 18$
3 standard reflections monitored every 200 reflections
intensity decay: none

Refinement

Refinement on *F*
$R = 0.0284$
$wR = 0.0257$
$S = 1.267$
1202 reflections
91 parameters
H atoms: C—H riding (see below)
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.0002$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ 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)*

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

	x	y	z	U_{eq}
W(1)	0.14269 (3)	1/4	0.40718 (2)	0.0443 (1)
Si(1)	0.3193 (3)	1/4	0.6136 (2)	0.0536 (8)
O(1)	0.2441 (4)	0.1375 (4)	0.3866 (3)	0.067 (2)
C(1)	−0.0123 (8)	1/4	0.2826 (6)	0.047 (3)
C(2)	−0.0527 (6)	0.1567 (5)	0.3337 (4)	0.043 (2)
C(3)	−0.1080 (5)	0.1931 (5)	0.4182 (4)	0.043 (2)
C(4)	0.0554 (9)	1/4	0.1882 (6)	0.065 (3)
C(5)	−0.0377 (7)	0.0429 (6)	0.3020 (5)	0.075 (3)
C(6)	−0.1714 (6)	0.1225 (7)	0.4926 (5)	0.071 (2)
C(7)	0.1427 (9)	1/4	0.5544 (6)	0.047 (2)
C(8)	0.290 (1)	1/4	0.7408 (7)	0.084 (4)
C(9)	0.4219 (7)	0.1274 (7)	0.5828 (5)	0.082 (3)

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

CP refers to the unweighted centroid of the cyclopentadienyl ring.

W(1)—O(1)	1.717 (4)	Si(1)—C(9)	1.855 (8)
W(1)—C(1)	2.321 (8)	C(1)—C(2)	1.424 (8)
W(1)—C(2)	2.424 (6)	C(1)—C(4)	1.51 (1)
W(1)—C(3)	2.477 (4)	C(2)—C(3)	1.403 (7)
W(1)—C(7)	2.128 (8)	C(2)—C(5)	1.488 (9)
W(1)···*CP*	2.11	C(3)—C(3^i)	1.41 (1)
Si(1)—C(7)	1.876 (8)	C(3)—C(6)	1.510 (8)
Si(1)—C(8)	1.86 (1)		
O(1)—W(1)—O(1^i)	108.5 (3)	C(2)—C(1)—C(4)	125.7 (4)
O(1)—W(1)—C(7)	100.0 (2)	C(1)—C(2)—C(3)	106.9 (6)
O(1)—W(1)—*CP*	117.7	C(1)—C(2)—C(5)	125.7 (6)
C(7)—W(1)—*CP*	110.0	C(3)—C(2)—C(5)	127.4 (6)
C(7)—Si(1)—C(8)	108.7 (4)	C(2)—C(3)—C(3^i)	108.7 (4)
C(7)—Si(1)—C(9)	110.8 (3)	C(2)—C(3)—C(6)	125.6 (6)
C(8)—Si(1)—C(9)	108.3 (3)	C(3^i)—C(3)—C(6)	125.4 (4)
C(9)—Si(1)—C(9^i)	109.8 (5)	Si(1)—C(7)—W(1)	117.1 (4)
C(2)—C(1)—C(2^i)	108.5 (7)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

H atoms were fixed in calculated positions with C—H = 0.98 Å and displacement parameters 20% greater than those of the parent atoms. C_5Me_5 methyl group orientations were based on difference map peak positions.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *DIRDIF* (Buerskens *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1161). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The First μ_4-Se Spiro-Type Fe_4Se_3 Cluster: $[(\mu\text{-}4\text{-}CH_3\text{-}C_6H_4Se)Fe_2(CO)_6]_2(\mu_4\text{-}Se)$

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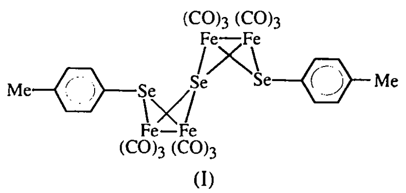
Abstract

In the molecule of the title cluster compound, μ_4-selenido-bis[μ-(4-tolylselenido)-hexacarbonyldiiron], two identical $(\mu\text{-}4\text{-}CH_3C_6H_4Se)Fe_2(CO)_6$ moieties are joined by a spiro-type four-coordinate Se atom, μ_4-Se. The four Se—Fe bond lengths around the central Se atom are 2.353 (3), 2.353 (3), 2.347 (3) and 2.358 (3) Å. The average (2.353 Å) is shorter than that (2.392 Å) of Se—Fe bond lengths formed between Fe atoms and the 4-tolylselenido ligands. In each diiron subcluster core, the 4-tolylselenido ligand is bridged between two Fe atoms.

Comment

In the course of our study on the reactions of alkylselenido-bridged anions $(\mu\text{-}R\text{Se})(\mu\text{-Se}^-)Fe_2(CO)_6$ (Song, Yan, Hu, Wang & Wang, 1995) with SO_2Cl_2, the title cluster, $[(\mu\text{-}4\text{-}CH_3C_6H_4Se)Fe_2(CO)_6]_2(\mu_4\text{-Se})$, (I), was isolated, which is the first spiro-type μ_4-Se cluster complex with an Fe_4Se_3 core.



(I)

The crystal of the title cluster is monoclinic and consists of discrete molecules. There are two crystallographically independent molecules in the asymmetric unit. However, only one set of bond lengths and angles are listed (Table 2) since those of the two independent molecules are essentially the same, the slight differences between them being considered as experimental error.

The molecule consists of two identical subclusters, $(\mu\text{-}4\text{-}CH_3C_6H_4Se)Fe_2(CO)_6$, joined together by a spiro-type four-coordinate Se atom, μ_4-Se, which is situated on the center of a distorted tetrahedron constructed by four Fe atoms; the 4-tolylselenido ligand $(\mu\text{-}SeC_6H_4CH_3\text{-}4)$ bridges two Fe atoms in each subcluster core. The structure is very similar to that of its sulfur analogs, $[(\mu\text{-}R\text{S})Fe_2(CO)_6]_2(\mu_4\text{-S})$ ($R = CH_3, C_2H_5$) (Coleman, Wojcicki, Pollick & Dahl, 1967; Song, Kadiata, Wang, Wang & Wang, 1988).

In this cluster compound, the bond distances between the μ_4-Se atom and the four Fe atoms are almost the same [Se(1)—Fe(1) 2.353 (3), Se(1)—Fe(2) 2.353 (3), Se(1)—Fe(3) 2.347 (3), Se(1)—Fe(4) 2.358 (3) Å], but slightly shorter than those between the Fe atoms and the bridging Se atoms attached to the tolyl groups [Se(2)—Fe(1) 2.392 (3) and Se(2)—Fe(2) 2.390 (4) Å; Se(3)—Fe(3) 2.386 (3) and Se(3)—Fe(4) 2.400 (4) Å]. This may mean that the bonds formed between Fe and μ_4-Se atoms are stronger than those formed between Fe and μ_2-Se atoms. The two Fe—Fe bond distances in

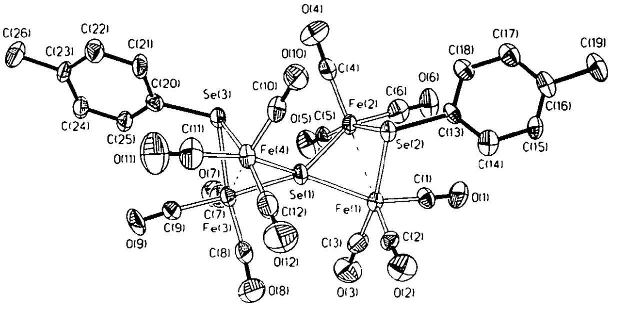


Fig. 1. Molecular structure of the title cluster showing 35% probability displacement ellipsoids. H atoms are omitted for clarity.