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{[(1*R*,2*S*,3*R*,6*R*)-2-(*tert*-Butyldimethylsilyloxymethyl)-6-(2-furyl)-3-methyl-4-oxocyclohexyl](methoxy)methylene}-pentacarbonyltungsten(0)

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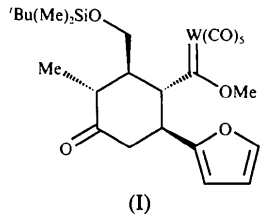
Abstract

The structure and absolute configuration of the title compound, [W(CO)$_5$(C$_{20}$H$_{32}$O$_4$Si)], is reported. The W atom has distorted octahedral coordination defined by one carbene and five carbonyl ligands.

Comment

Fischer-carbene complexes (Fischer & Maasbol, 1964) are well known for their ability to produce a wide range of reactions (Wulff *et al.*, 1990) which are used increasingly in organic synthesis. For example, they promote benzannulation reactions between α,β-unsaturated complexes and alkenes, cyclopropanation of olefins, cycloaddition of unsaturated complexes to 1,3-dienes, and photolytic reactions. In an earlier paper we reported (Barluenga *et al.*, 1994) a highly stereoselective [4+2] cycloaddition reaction between chiral 2-amino-1,3-dienes and α,β-unsaturated Fischer-carbene complexes of tungsten. Since the elucidation of the absolute configuration of these complexes is essential in order to understand the detailed mechanism of selective formation of one of the possible enantiomers, a single-crystal X-ray diffraction study of the title complex (I) has been carried out.



(I)

The complex contains a central W atom bonded to one carbene and five carbonyl groups. The W atom is thus coordinated by six C atoms with a W—C(carbene) bond length of 2.171 (3) Å and a mean W—C(CO) bond length of 2.037 (2) Å. The stereochemistry around the W atom is only approximately octahedral. The maximum distortions from ideal octahedral geometry are shown by the angles C23—W1—C25 and C1—W1—C22 of 85.1 (2) and 98.3 (2)°, respectively.

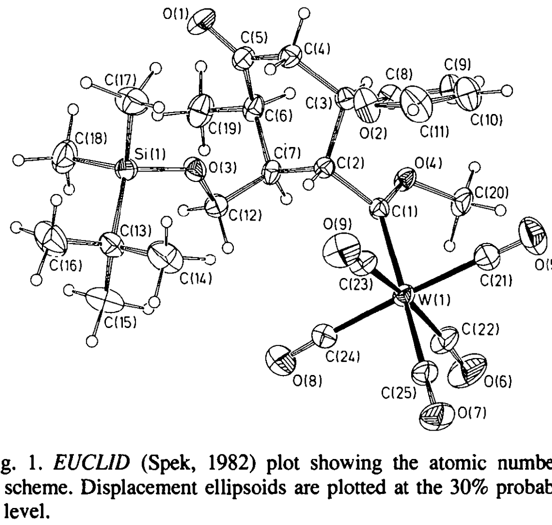


Fig. 1. *EUCLID* (Spek, 1982) plot showing the atomic numbering scheme. Displacement ellipsoids are plotted at the 30% probability level.

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Experimental

To a solution of 0.66 g (2.03 mmol) of (*S*)-(*E*)-*N*-{2-methyl-1-methylene-4-[(*tert*-butyldimethylsilyl)oxy]-2-butenyl}-2-(methoxymethyl)pyrrolidine in 20 ml of anhydrous DMF cooled to 223 K, 0.93 g of pentacarbonyl[*trans*-3-(2-furyl)-1-methoxy-2-propenylidene]tungsten(0) was added. The deep red solution was stirred for 2 days while the temperature slowly increased to 293 K. The reaction mixture was then concentrated and hydrolysed by filtration through silica gel with water-saturated diethyl ether. The orange solution was collected, concentrated and chromatographed on silica gel with hexane:ethyl acetate (3:1). Fractions of the *endo* adduct (1*R**,2*R**,3*S**,6*R**), with R_f 0.66 (250 mg, 18% yield, e.e. 2%), and the title compound, with R_f 0.52 {90 mg, 6.5% yield, $[\alpha]_D^{20}$ -27° (CH_2Cl_2), *c* 2.15×10^{-3} g ml^{-1}, e.e. 98%}, were collected. The second fraction was crystallized from hexane (m.p. 391–393 K).

Crystal data

$[W(CO_5)(C_{20}H_{32}O_4Si)]$
$M_r = 688.45$
Orthorhombic
$P2_12_12_1$
$a = 8.807$ (19) Å
$b = 15.163$ (5) Å
$c = 21.468$ (44) Å
$V = 2866.9$ (85) Å^3
$Z = 4$
$D_x = 1.595$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15–20°$
$\mu = 4.117$ mm^{-1}
$T = 293$ (2) K
Transparent blocks
0.40 × 0.23 × 0.23 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: semi-empirical (*DIFABS*: Walker & Stuart, 1983)
$T_{min} = 0.95$, $T_{max} = 1.16$
5788 measured reflections
5038 independent reflections (including Friedel pairs)

4558 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.029$
$\theta_{max} = 24.99°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 18$
$l = -25 \rightarrow 25$
3 standard reflections
frequency: 60 min
intensity variation: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0178$
$wR(F^2) = 0.0469$
$S = 1.099$
5038 reflections
347 parameters
H atoms riding with common U_{iso}
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0255P)^2 + 0.9420P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.173$
$\Delta\rho_{max} = 0.588$ e Å^{-3}
$\Delta\rho_{min} = -0.352$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
W1	−0.12121 (2)	−0.130624 (8)	−0.065055 (7)	0.04024 (5)
Si1	−0.57893 (12)	0.15575 (7)	−0.20461 (5)	0.0454 (3)
C1	−0.0841 (4)	0.0104 (2)	−0.0561 (2)	0.0345 (7)
O4	0.0342 (3)	0.0553 (2)	−0.03714 (13)	0.0438 (6)
O3	−0.4264 (3)	0.1349 (2)	−0.16281 (11)	0.0464 (6)
O2	−0.4364 (4)	0.0623 (3)	0.03774 (15)	0.0655 (9)
C2	−0.2056 (4)	0.0796 (2)	−0.0711 (2)	0.0342 (7)
C24	−0.1425 (5)	−0.1181 (3)	−0.1587 (2)	0.0543 (10)
C8	−0.2896 (5)	0.0895 (3)	0.0407 (2)	0.0440 (9)
C22	0.0964 (5)	−0.1675 (3)	−0.0820 (2)	0.0592 (12)
O1	−0.3498 (5)	0.3353 (2)	−0.1023 (2)	0.0741 (10)
C12	−0.2801 (4)	0.1072 (3)	−0.1828 (2)	0.0453 (9)
C7	−0.1660 (3)	0.1302 (3)	−0.1323 (2)	0.0384 (7)
C5	−0.2892 (5)	0.2670 (3)	−0.0878 (2)	0.0471 (9)
C25	−0.1739 (5)	−0.2603 (3)	−0.0706 (2)	0.0542 (10)
O7	−0.2050 (5)	−0.3336 (2)	−0.0726 (2)	0.0837 (11)
O6	0.2127 (5)	−0.1956 (3)	−0.0929 (2)	0.1009 (15)
C6	−0.1531 (4)	0.2307 (2)	−0.1226 (2)	0.0455 (9)
O9	−0.4767 (4)	−0.1098 (3)	−0.0460 (2)	0.0902 (13)
C9	−0.2258 (6)	0.0621 (3)	0.0936 (2)	0.0583 (11)
C21	−0.0876 (6)	−0.1457 (3)	0.0288 (2)	0.0606 (12)
C4	−0.3398 (4)	0.2161 (3)	−0.0323 (2)	0.0472 (10)
C3	−0.2326 (4)	0.1415 (3)	−0.0142 (2)	0.0402 (8)
O5	−0.0676 (5)	−0.1540 (3)	0.0804 (2)	0.0927 (14)
C15	−0.5555 (7)	0.0135 (4)	−0.2888 (3)	0.081 (2)
C10	−0.3384 (6)	0.0131 (4)	0.1261 (2)	0.0731 (15)
C13	−0.6599 (5)	0.0517 (3)	−0.2393 (2)	0.0515 (10)
C23	−0.3502 (4)	−0.1122 (3)	−0.0521 (2)	0.0548 (10)
C18	−0.5312 (8)	0.2370 (4)	−0.2670 (3)	0.079 (2)
O8	−0.1487 (6)	−0.1123 (3)	−0.2114 (2)	0.0922 (12)
C19	−0.1207 (7)	0.2821 (3)	−0.1822 (2)	0.0646 (11)
C11	−0.4611 (7)	0.0143 (4)	0.0912 (2)	0.080 (2)
C17	−0.7104 (6)	0.2032 (4)	−0.1459 (3)	0.080 (2)
C20	0.1705 (4)	0.0118 (3)	−0.0142 (2)	0.0545 (11)
C14	−0.6852 (9)	−0.0171 (4)	−0.1882 (3)	0.096 (2)
C16	−0.8153 (7)	0.0724 (5)	−0.2699 (3)	0.094 (2)

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

W1—C25	2.023 (4)	C8—C9	1.333 (6)
W1—C24	2.028 (6)	C8—C3	1.504 (6)
W1—C22	2.029 (6)	C22—O6	1.134 (6)
W1—C21	2.049 (6)	O1—C5	1.206 (5)
W1—C23	2.055 (6)	C12—C7	1.518 (5)
W1—C1	2.171 (3)	C7—C6	1.543 (5)
Si1—O3	1.646 (4)	C5—C4	1.488 (6)
Si1—C17	1.857 (5)	C5—C6	1.516 (6)
Si1—C18	1.868 (6)	C25—O7	1.146 (5)
Si1—C13	1.884 (4)	C6—C19	1.525 (6)
C1—O4	1.309 (4)	O9—C23	1.122 (6)
C1—C2	1.534 (5)	C9—C10	1.422 (7)
O4—C20	1.456 (5)	C21—O5	1.129 (6)
O3—C12	1.422 (5)	C4—C3	1.524 (5)
O2—C8	1.358 (5)	C15—C13	1.520 (7)
O2—C11	1.377 (6)	C10—C11	1.314 (8)
C2—C3	1.559 (5)	C13—C14	1.531 (7)
C2—C7	1.560 (5)	C13—C16	1.550 (7)
C24—O8	1.135 (5)		
C25—W1—C24	90.6 (2)	C9—C8—O2	110.3 (4)
C25—W1—C22	86.5 (2)	C9—C8—C3	133.6 (4)
C24—W1—C22	86.3 (2)	O2—C8—C3	116.1 (4)
C25—W1—C21	89.0 (2)	O6—C22—W1	173.5 (4)
C24—W1—C21	176.8 (2)	O3—C12—C7	108.5 (3)
C22—W1—C21	90.5 (2)	C12—C7—C6	111.9 (3)
C25—W1—C23	85.1 (2)	C12—C7—C2	109.9 (3)
C24—W1—C23	91.7 (2)	C6—C7—C2	112.8 (3)
C22—W1—C23	171.3 (2)	O1—C5—C4	121.4 (4)
C21—W1—C23	91.4 (2)	O1—C5—C6	122.3 (4)
C25—W1—C1	175.1 (2)	C4—C5—C6	116.3 (3)

C24—W1—C1	90.59 (14)	O7—C25—W1	178.6 (5)
C22—W1—C1	98.3 (2)	C5—C6—C19	112.1 (4)
C21—W1—C1	90.01 (15)	C5—C6—C7	111.5 (3)
C23—W1—C1	90.13 (15)	C19—C6—C7	113.9 (4)
O3—Si1—C17	102.3 (2)	C8—C9—C10	106.6 (5)
O3—Si1—C18	109.5 (2)	O5—C21—W1	179.4 (5)
C17—Si1—C18	111.8 (3)	C5—C4—C3	113.8 (3)
O3—Si1—C13	111.3 (2)	C8—C3—C4	112.4 (3)
C17—Si1—C13	110.9 (3)	C8—C3—C2	110.5 (3)
C18—Si1—C13	110.7 (3)	C4—C3—C2	110.0 (3)
O4—C1—C2	105.3 (3)	C11—C10—C9	106.7 (4)
O4—C1—W1	131.3 (2)	C15—C13—C14	109.2 (5)
C2—C1—W1	123.4 (2)	C15—C13—C16	108.3 (4)
C1—O4—C20	121.7 (3)	C14—C13—C16	108.2 (5)
C12—O3—Si1	129.2 (2)	C15—C13—Si1	111.6 (3)
C8—O2—C11	105.8 (4)	C14—C13—Si1	110.0 (3)
C1—C2—C3	110.7 (3)	C16—C13—Si1	109.4 (4)
C1—C2—C7	111.0 (3)	O9—C23—W1	174.0 (4)
C3—C2—C7	113.5 (3)	C10—C11—O2	110.6 (5)
O8—C24—W1	177.3 (5)		

Data were collected with profile analysis over all reflections (Lehman & Larsen, 1974; Grant & Gabe, 1978). Cell refinement was performed using *CRYSDA DIRDIF* (Beurskens *et al.*, 1992). The local program *DATAR* was used for data reduction. The structure was solved by Patterson interpretation using the program *SHELXS*86 (Sheldrick, 1990). Refinement was performed using *SHELX*76 (Sheldrick, 1976; Van der Maelen Uría, 1991) and *SHELXL*93 (Sheldrick, 1993). The absolute configuration was tested using the program *BIJVOET* (Beurskens, Noordik & Beurskens, 1980) giving B = 1.0000 (1) for the 200 Friedel pairs showing the largest intensity differences. The material for publication was prepared using *SHELXL*93 and *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A (Phenyldithiocarbamato)rhodatelluraborane Compound: [2-{η^2-S$_2$CN(H)Ph}-2-(PPh$_3$)-*closo*-2,1-RhTeB$_{10}$H$_{10}$]

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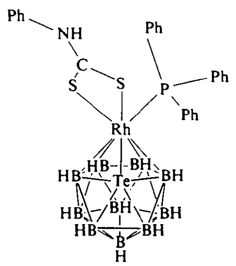
Abstract

The Rh atom in 2-(N-phenyldithiocarbamato-S,S')-2-(triphenylphosphine)-*closo*-2,1-rhodatelluradodecaborane(12), [Rh(C$_7$H$_6$NS$_2$)(C$_{18}$H$_{15}$P)(B$_{10}$H$_{10}$Te)], is bonded to triphenylphosphine [Rh—P 2.4020 (5) Å], N-phenyldithiocarbamate [Rh—S 2.4132 (5) and 2.3577 (6) Å] and the TeB$_4$ face of the TeB$_{10}$H$_{10}$ ligand [Rh—Te 2.5812 (3) Å].

Comment

The title compound was prepared by the reaction of excess PhNCS with [2,2-(PPh$_3$)$_2$-2-H-1,2-TeRhB$_{10}$H$_{10}$] in CH$_2$Cl$_2$ solution. The X-ray analysis was undertaken to establish the nature of the sulfur-containing ligand and its mode of bonding. Our analysis shows that the Rh atom in the title compound, (I), is bonded to PPh$_3$ and η^2-S$_2$CNHPh ligands as well as to the TeB$_4$ face of the TeB$_{10}$H$_{10}$ cage. The twelve-vertex distorted *closo* dodecahedral cage can be described in terms of Wade's rules as a variation of *closo*-[B$_{12}$H$_{12}$]$^{2-}$ with the Rh(η^2-S$_2$CNHPh)(PPh$_3$) unit equivalent to BH and the Te atom to [BH]$^{2-}$ (Wade, 1976). The Rh—Te bond length of 2.5812 (3) Å is significantly shorter than that of 2.6172 (4) Å in [2,2-(PPh$_3$)$_2$-2-H-1,2-TeRhB$_{10}$H$_{10}$] (Faridoon *et al.*, 1988). The Rh—S



(I)

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