C(18)—N(1)—C(17)	119.2 (4)	C(20)—C(19)—C(18)	109.0 (3)
C(38)—N(2)—C(34)	122.7 (5)	C(19)—C(20)—C(21)	111.8 (4)
C(39)—N(2)—C(34)	118.7 (4)	C(22)—C(21)—C(20)	112.4 (4)
C(39)—N(2)—C(38)	118.6 (5)	C(21)—C(22)—C(23)	114.3 (4)
C(6)—C(1)—O(1)	127.3 (4)	C(24)—C(23)—C(22)	113.1 (4)
C(2)—C(1)—O(1)	111.3 (4)	C(23)—C(24)—C(25)	114.9 (4)
C(2)—C(1)—C(6)	121.4 (4)	C(24)—C(25)—C(26)	113.9 (4)
C(3)—C(2)—O(2)	126.6 (4)	C(27)—C(26)—C(25)	114.6 (4)
C(1)—C(2)—O(2)	112.3 (3)	C(28)—C(27)—C(26)	113.4 (4)
C(1)—C(2)—C(3)	121.1 (4)	C(29)—C(28)—C(27)	113.9 (4)
C(4)—C(3)—C(2)	120.4 (4)	C(28)—C(29)—C(30)	113.3 (4)
Cl(1)—C(3)—C(2)	120.5 (3)	C(31)—C(30)—C(29)	114.3 (4)
Cl(1)—C(3)—C(4)	119.0 (3)	C(30)—C(31)—C(32)	113.0 (4)
C(3)—C(4)—O(3)	125.2 (4)	C(33)—C(32)—C(31)	114.9 (5)
C(5)—C(4)—O(3)	116.7 (4)	C(35)—C(34)—N(2)	118.9 (5)
C(5)—C(4)—C(3)	118.0 (4)	C(36)—C(35)—C(34)	122.5 (7)
C(6)—C(5)—O(4)	124.9 (4)	C(37)—C(36)—C(35)	119.8 (7)
C(4)—C(5)—O(4)	117.1 (4)	C(38)—C(37)—C(36)	117.5 (6)
C(4)—C(5)—C(6)	117.9 (4)	C(37)—C(38)—N(2)	118.6 (5)
C(5)—C(6)—C(1)	120.1 (4)	C(40)—C(39)—N(2)	110.4 (5)
Cl(2)—C(6)—C(1)	120.8 (3)	C(39)—C(40)—C(41)	114.5 (4)
Cl(2)—C(6)—C(5)	119.0 (3)	C(40)—C(41)—C(42)	114.9 (4)
C(12)—C(7)—O(5)	127.3 (4)	C(41)—C(42)—C(43)	115.0 (4)
C(8)—C(7)—O(5)	111.5 (4)	C(42)—C(43)—C(44)	117.1 (5)
C(8)—C(7)—C(12)	121.2 (4)	C(43)—C(44)—C(45)	117.3 (5)
C(9)—C(8)—O(6)	126.5 (4)	C(44)—C(45)—C(46)	118.4 (5)
C(7)—C(8)—O(6)	112.2 (3)	C(47)—C(46)—C(45)	117.1 (5)
C(7)—C(8)—C(9)	121.2 (4)	C(46)—C(47)—C(48)	117.3 (5)
C(10)—C(9)—C(8)	120.4 (4)	C(47)—C(48)—C(49)	117.8 (5)
Cl(3)—C(9)—C(8)	121.6 (3)	C(50)—C(49)—C(48)	118.5 (5)
Cl(3)—C(9)—C(10)	118.0 (3)	C(49)—C(50)—C(51)	117.0 (5)
C(9)—C(10)—O(7)	124.7 (4)	C(50)—C(51)—C(52)	117.0 (5)
C(11)—C(10)—O(7)	117.0 (4)	C(51)—C(52)—C(53)	117.2 (6)
C(11)—C(10)—C(9)	118.3 (4)	C(52)—C(53)—C(54)	122.5 (7)
C(12)—C(11)—O(8)	124.6 (4)	O(2)—Be(1)—O(5)	116.6 (4)
C(10)—C(11)—O(8)	117.4 (4)	O(6)—Be(1)—O(5)	98.6 (4)
C(10)—C(11)—C(12)	118.0 (4)	O(6)—Be(1)—O(2)	113.8 (3)
C(11)—C(12)—C(7)	120.4 (4)	O(1)—Be(1)—O(5)	117.8 (3)
Cl(4)—C(12)—C(7)	120.8 (3)	O(1)—Be(1)—O(2)	98.2 (4)
Cl(4)—C(12)—C(11)	118.7 (3)	O(1)—Be(1)—O(6)	112.8 (4)

The single crystals of this compound tend to be twinned, therefore, only a very small sample could be measured, resulting in a very high number of unobserved reflections. This is the reason for the difference between unweighted and weighted R values. The ratio could be improved by using only $F > 3\sigma(F)$ data, but then the reflections/parameter ratio would deteriorate.

One common isotropic displacement parameter for the H atoms was used. All H-atom positions could be recognized in difference Fourier maps. The refinement was carried out by the newly-developed Levenberg–Marquardt least-squares algorithm *LQFLEV* (Spengler & Zimmermann, 1994) using the second derivatives of the structure factors.

Data collection: local software (Gomm, 1993). Cell refinement: local software (Gomm, 1993). Data reduction: local software (Gomm, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTAN* (Burzlaff & Rothammel, 1988). Software used to prepare material for publication: *CRYSTAN*.

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(η^5-Cyclopentadienyl)[2-(1,1-diphenyl-ethyl-C^2)phenyl-C^1]oxo(trimethylsilyl-methylthio)tungsten, [WO(C4H11SSi)-(C5H5)(C20H16)]

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Abstract

Treatment of [CpW(NO)(CH2SiMe3)(CH2CPh3)] with sulfur produces [CpW(O)(SCH2SiMe3)(CH2CPh2-C6H4)], in which S is inserted in one W—C bond, but in addition, replacement of NO by O and orthometallation have occurred.

Comment

In a study of the reactions of the mixed alkyl complex CpW(NO)(CH2SiMe3)(CH2CPh3) (Brunet, Debad, Legzdins, Trotter, Veltheer & Yee, 1993), treatment with sulfur was found to give only one isolable product in very low yield. The present analysis has established the structure of this product, (I), as [CpW(O)(SCH2SiMe3)(CH2CPh2C6H4)]. Sulfur has been inserted preferentially into one of the W—C(alkyl) bonds, but in addition, the nitrosyl group has been replaced by an oxo ligand and orthometallation has occurred.


(I)
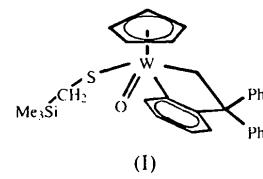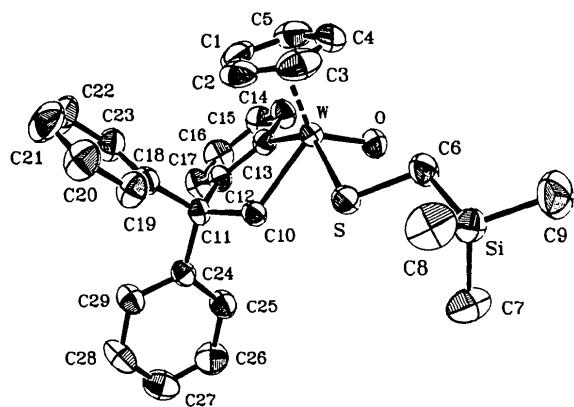
Fig. 1. View of the molecule (50% probability ellipsoids).

Experimental

The method of synthesis of the title complex is that described by Brunet (1988) and has been deposited.

Crystal data

[WO(C₄H₁₁SSi)(C₅H₅)-
(C₂₀H₁₆)]
$M_r = 640.57$
Triclinic
$P\bar{1}$
$a = 9.415\ (2)$ Å
$b = 11.539\ (3)$ Å
$c = 13.388\ (2)$ Å
$\alpha = 72.18\ (1)°$
$\beta = 79.37\ (1)°$
$\gamma = 76.90\ (3)°$
$V = 1338.2\ (5)$ Å³
$Z = 2$
$D_x = 1.60$ Mg m⁻³

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25
reflections
$\theta = 21.9–23.1°$
$\mu = 4.57$ mm⁻¹
$T = 294$ K
Plate
$0.51 \times 0.20 \times 0.08$ mm
Orange

Data collection

Enraf–Nonius CAD-4F
diffractometer
$\omega/2\theta$ scans
Absorption correction:
analytical (de Meulenaer
& Tompa, 1965)
$T_{min} = 0.32$, $T_{max} = 0.70$
6097 measured reflections
6097 independent reflections

5059 observed reflections
$[I > 3\sigma(I)]$
$\theta_{max} = 27.5°$
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -17 \rightarrow 0$
3 standard reflections
monitored every 150
reflections
intensity decay: 6.0%

Refinement

Refinement on F
$R = 0.027$
$wR = 0.032$
$S = 1.25$
5059 reflections
298 parameters
H-atom parameters not
refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.05$
$\Delta\rho_{max} = 1.9$ e Å⁻³
$\Delta\rho_{min} = -1.1$ 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* (Å²)

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

	x	y	z	U_{eq}
W	0.28980 (2)	0.01377 (1)	0.16476 (1)	0.032
S	0.19993 (12)	0.20583 (9)	0.21432 (8)	0.042
Si	0.20743 (15)	0.47831 (11)	0.12039 (11)	0.050
O	0.4570 (3)	0.0530 (3)	0.1107 (2)	0.045
C1	0.1403 (7)	-0.1153 (5)	0.1307 (5)	0.067
C2	0.0393 (5)	-0.0165 (7)	0.1532 (4)	0.067
C3	0.0722 (7)	0.0899 (5)	0.0775 (5)	0.071
C4	0.1884 (7)	0.0564 (7)	0.0070 (4)	0.075
C5	0.2342 (6)	-0.0686 (6)	0.0403 (4)	0.064
C6	0.2465 (6)	0.3228 (4)	0.0932 (4)	0.053
C7	0.3057 (7)	0.4703 (6)	0.2294 (5)	0.076
C8	0.0065 (7)	0.5250 (6)	0.1557 (6)	0.083
C9	0.2730 (9)	0.5906 (6)	-0.0028 (6)	0.090
C10	0.2471 (4)	-0.0290 (3)	0.3399 (3)	0.035
C11	0.2475 (4)	-0.1659 (3)	0.4040 (3)	0.034
C12	0.3684 (4)	-0.2360 (4)	0.3414 (3)	0.036
C13	0.3983 (4)	-0.1753 (4)	0.2341 (3)	0.036
C14	0.5104 (5)	-0.2353 (4)	0.1725 (3)	0.046
C15	0.5905 (5)	-0.3505 (5)	0.2150 (4)	0.053
C16	0.5602 (5)	-0.4096 (4)	0.3213 (4)	0.052
C17	0.4500 (5)	-0.3528 (4)	0.3836 (3)	0.046
C18	0.0982 (4)	-0.2034 (4)	0.4099 (3)	0.039
C19	-0.0333 (5)	-0.1217 (4)	0.4254 (4)	0.051
C20	-0.1674 (5)	-0.1513 (6)	0.4293 (5)	0.067
C21	-0.1759 (6)	-0.2662 (7)	0.4203 (6)	0.082
C22	-0.0498 (6)	-0.3474 (6)	0.4073 (6)	0.076
C23	0.0874 (5)	-0.3176 (4)	0.4031 (4)	0.053
C24	0.2848 (4)	-0.1837 (4)	0.5160 (3)	0.037
C25	0.4203 (5)	-0.1622 (4)	0.5268 (3)	0.047
C26	0.4572 (6)	-0.1738 (5)	0.6249 (4)	0.060
C27	0.3600 (6)	-0.2063 (6)	0.7148 (4)	0.065
C28	0.2266 (6)	-0.2288 (5)	0.7062 (3)	0.060
C29	0.1890 (5)	-0.2196 (4)	0.6071 (3)	0.048
Cp†	0.1349	-0.0108	0.0817	0.07

† Cp is the centroid of cyclopentadienyl ring.

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

W—S	2.431 (1)	S—C6	1.819 (5)
W—O	1.706 (3)	Si—C6	1.881 (5)
W—C10	2.222 (3)	Si—C7	1.836 (6)
W—C13	2.183 (4)	Si—C8	1.859 (6)
W—Cp	2.103 (3)	Si—C9	1.860 (7)
S—W—O	92.7 (1)	C6—Si—C7	109.7 (3)
S—W—C10	70.9 (1)	C6—Si—C8	109.7 (3)
S—W—C13	138.7 (1)	C6—Si—C9	107.2 (3)
S—W—Cp	108.6 (1)	C7—Si—C8	109.9 (3)
O—W—C10	115.0 (1)	C7—Si—C9	110.3 (3)
O—W—C13	89.7 (1)	C8—Si—C9	110.0 (3)
O—W—Cp	125.6 (1)	S—C6—Si	109.4 (2)
C10—W—C13	70.8 (1)	W—C10—C11	117.9 (2)
C10—W—Cp	119.2 (1)	W—C13—C12	121.9 (3)
C13—W—Cp	103.2 (1)	W—C13—C14	119.7 (3)
W—S—C6	102.9 (2)		

The structure was determined by Patterson methods.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, and details of synthesis and a packing diagram have been deposited with the IUCr (Reference: BK1047). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Tetraphenylporphyrinato)zirconium(IV) Diacetate

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Abstract

The title compound, bis(acetato-O,O')[5,10,15,20-tetraphenyl-$21H,23H$-porphinato(2−)-$N^{21},N^{22},N^{23},N^{24}$]zirconium, [Zr(C$_2H_3O_2$)$_2$(C$_{44}H_{28}N_4$)].CH$_2Cl_2$, crystallizes in space group $C2/c$ with $Z = 4$. The two acetate ligands are coordinated in a mutually cis configuration and the geometry about the Zr center approximates a square antiprism. The distance of the Zr atom from the porphyrin plane is 1.036 (7) Å. The average Zn—N and Zr—O bond distances are 2.257 (7) and 2.260 (6) Å, respectively, and the average C$_{carbonyl}$—Zr—C$_{carbonyl}$ and N—Zr—N($-x$, y, $\frac{1}{2}-z$) angles are 85.1 (4) and 125.4 (3)°, respectively.

Comment

The title compound, [(TPP)Zr(OAc)$_2$], was prepared by the reaction of (5,10,15,20-tetraphenylporphyrinato)zirconium(IV) dichloride with a refluxing mixture of acetic acid and pyridine (1:1.5), and crystallized by the addition of boiling H$_2$O. The diacetate was recrystallized from CH$_2$Cl$_2$–heptane solution (1:1) as the CH$_2$Cl$_2$ solvate. This procedure is similar to that described for the preparation of (2,3,7,8,12,13,17,18-octaethylporphyrinato)zirconium(IV) diacetate [(OEP)-Zr(OAc)$_2$] (Buchler et al., 1971), the structure of which has been briefly mentioned and shows the metal to be eight-coordinate with bidentate cis acetate ligands (Hoard, 1975).

[(TPP)Zr(OAc)$_2$]   TPP^2
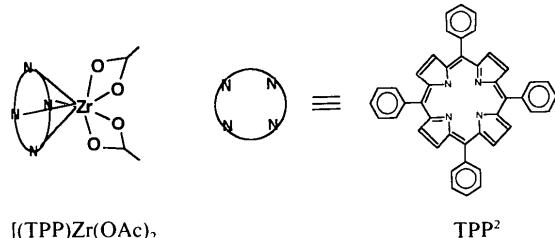
Related compounds which have been crystallographically characterized are [(OEP)Zr(CH$_2$SiMe$_3$)$_2$] (Brand & Arnold, 1992), [(TPP)ZrCl$_2$(thf)] (Kim, Whang, Kim & Do, 1993), [(OEP)ZrCl$_2$], [(OEP)Zr(O^{t}Bu)$_2$] and [(OEP)ZrMe$_2$].CH$_2$Cl$_2$ (Brand & Arnold, 1993).

Group IV d^0 metalloporphyrins with cis coordination of ligands are of interest because of the potential analogy to Group IV d^0 metallocenes, the Ziegler–Natta catalysts that promote polymerization of ethylenes and propylene.
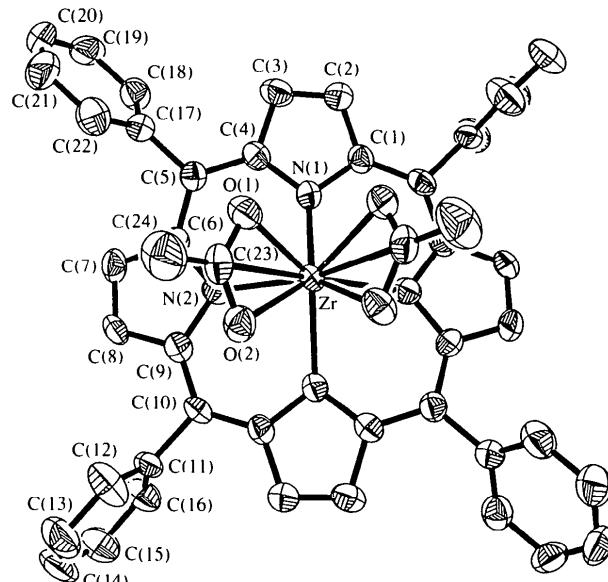

Fig. 1. Displacement ellipsoid drawing (SHELXTL-Plus; Sheldrick, 1991) of the title molecule. Ellipsoids enclose 50% probability and H atoms have been omitted. The molecule has twofold rotational symmetry.