

N1	0.4015 (3)	0.7567 (2)	0.3091 (2)	0.0363 (5)
C1	0.3065 (3)	0.7369 (3)	0.3753 (2)	0.0374 (7)
C2	0.3463 (4)	0.7604 (3)	0.4598 (2)	0.0503 (8)
C3	0.2556 (5)	0.7353 (4)	0.5253 (3)	0.0692 (12)
C4	0.1249 (5)	0.6859 (5)	0.5087 (3)	0.079 (2)
C5	0.0832 (4)	0.6649 (5)	0.4271 (3)	0.0704 (13)
C6	0.1725 (4)	0.6887 (4)	0.3598 (3)	0.0514 (9)
C7	0.3110 (4)	0.9320 (6)	0.0714 (2)	0.0698 (13)
C8	0.1585 (4)	0.9520 (5)	0.0456 (2)	0.0579 (10)
C9	0.0827 (4)	0.9704 (5)	0.1270 (3)	0.0627 (11)
C10	0.1688 (4)	0.9006 (5)	0.1893 (3)	0.0647 (12)
C11	0.6223 (4)	0.4341 (4)	0.0962 (2)	0.0496 (8)
C12	0.7460 (6)	0.3513 (6)	0.0864 (3)	0.0768 (14)
C13	0.8101 (5)	0.3348 (5)	0.1727 (3)	0.0683 (11)
C14	0.6901 (6)	0.3618 (4)	0.2300 (3)	0.0684 (12)

Table 2. Selected geometric parameters (Å, °)

Zr1—N1	2.068 (2)	Zr2—N1	2.051 (2)
Zr1—O1	2.216 (2)	Zr2—O2	2.325 (2)
Zr1—Cl1	2.5141 (10)	Zr2—Cl2	2.4880 (11)
Zr1...Zr2	3.1466 (8)	N1—Cl1	1.407 (4)
N1'—Zr1—N1	79.98 (14)	N1—Zr2—O2	178.14 (9)
N1—Zr1—O1'	99.31 (9)	O2'—Zr2—O2	79.19 (12)
N1—Zr1—O1	90.75 (9)	N1—Zr2—Cl2	97.51 (7)
O1'—Zr1—O1	166.89 (13)	N1'—Zr2—Cl2	93.75 (7)
N1—Zr1—Cl1'	92.00 (7)	O2'—Zr2—Cl2	84.50 (6)
N1—Zr1—Cl1	169.98 (7)	O2—Zr2—Cl2	84.11 (6)
O1'—Zr1—Cl1	86.69 (7)	Cl2'—Zr2—Cl2	165.19 (5)
O1—Zr1—Cl1	84.59 (6)	C1—N1—Zr2	121.2 (2)
Cl1'—Zr1—Cl1	96.56 (6)	C1—N1—Zr1	139.0 (2)
N1—Zr2—N1'	80.80 (14)	Zr2—N1—Zr1	99.61 (10)
N1—Zr2—O2'	100.03 (9)		

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

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993b). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1234). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Bradley, D. C. & Chisholm, M. H. (1976). *Acc. Chem. Res.* **9**, 273–280.
- Fay, R. C. (1987). *Comprehensive Coordination Chemistry*, edited by G. Wilkinson, R. D. Gillard & J. A. McCleverty, Vol. 3, pp. 371–376. Oxford: Pergamon Press.
- Kotke, T. & Stalke, D. (1993). *J. Appl. Cryst.* **26**, 615–619.
- Molecular Structure Corporation (1993a). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1993b). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6c. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Nugent, W. A. & Harlow, R. L. (1979). *Inorg. Chem.* **18**, 2030–2032.
- Sheldrick, G. M. (1990). *SHELXTL/PC*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1996). **C52**, 1084–1086

Tricarbonyl(cyclopentadienyl)(selenotriphenylphosphonium)tungsten(I) Perchlorate, [W(C₅H₅)(C₁₈H₁₅PSe)(CO)₃](ClO₄)

CARSTEN THÖNE AND PETER G. JONES

Institut für Analytische und Anorganische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: p.jones@tu-bs.de

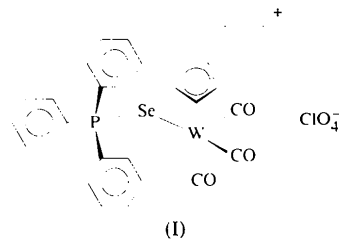
(Received 21 September 1995; accepted 8 November 1995)

Abstract

The P—Se bond length of 2.194 (1) Å indicates selenophosphonium character, rather than that of a triphenylphosphine selenide complex. The W atom displays 'piano-stool' coordination with a W—Se bond length of 2.658 (1) Å.

Comment

Recently, we reported the first crystal structure of an organoselenophosphonium salt, namely [Ph₃PSeMe]⁺(ClO₄)⁻ (Jones & Thöne, 1994). This compound was obtained by the reaction of Ph₃PAuCl with Me₂Se₂ in the presence of AgClO₄. An analogous reaction employing the organotungsten diselenide [Cp(CO)₃W]₂Se₂ (Cp is η⁵-cyclopentadienyl) instead of Me₂Se₂ led to the title compound, (I), in low yield.



The cation is shown in Fig. 1; the structure of the selenophosphonium moiety is very similar to that in [Ph₃PSeMe]⁺. The Se atom displays slightly distorted pseudo-tetrahedral geometry [P—Se(1)—W(1) 111.43 (4)°], and the P—Se bond length of 2.194 (1) Å is only slightly shorter than that of 2.205 (2) Å observed in [Ph₃PSeMe]⁺. Corresponding P—Se bond lengths in λ⁵-organoselenophosphoranes are considerably longer [2.273 (2) Å in (MeO)P(Se)C(CF₃)₂N=CNMe₂ (Burger, Ottlinger, Frank & Schubert, 1978), 2.243 (1) Å in (p-O₂NPhO)-(Ph)(p-ClPhSe)P(NMe)C(=O)NMe and 2.239 (2) Å in (PhSe)(Cl)(Me)P(NMe)C(=O)NPh (Pinchuk, Müller, Thönnessen, Shermolovich, Jones & Schmutzler, 1995)].

In contrast, coordinated Ph_3PSe in metal complexes shows shorter P—Se bonds because of more pronounced double-bond character in coordinative bonds {e.g. 2.174 (1) Å in $[(\text{Ph}_3\text{PSe})_2\text{Au}](\text{SbF}_6)$ and $\text{Ph}_3\text{PSeAuC}_6\text{F}_5$ (Jones & Thöne, 1991*a,b*), 2.169 (6) Å in $[(\text{Ph}_3\text{PSe})\text{HgCl}_2]_2$ (Glasser, Ingram, King & McQuillan, 1969)}, whereas in uncoordinated phosphine selenides, the P—Se bonds are *ca* 0.07 Å shorter [2.106 (1) (Coddling & Kerr, 1979), 2.111 (1) and 2.114 (1) Å (Jones, Kienitz & Thöne, 1994) in two modifications of Ph_3PSe , 2.103 (1) Å in $\text{dppm}(\text{Se})$ (Colton, Hoskins & Panagiotidou, 1987)]. From these observations, we conclude that the cation of the title compound represents more 'selenophosphonium' character than usual coordinative bonding by the Se donor atom and thus prefer the title formulation to that of a triphenylphosphine selenide complex.

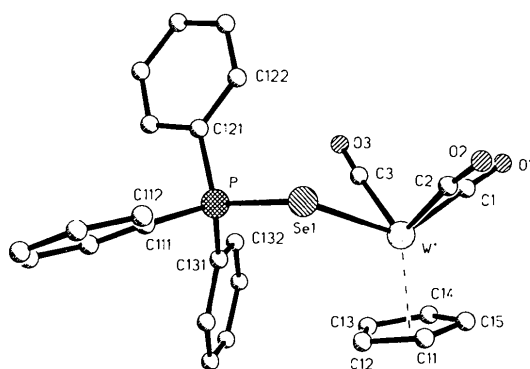


Fig. 1. The cation of the title compound in the crystal. All atoms are drawn as spheres of arbitrary radii.

The organotungsten moiety of the structure shows a 'piano-stool' arrangement, as in many other $M(\text{C}_5\text{H}_5)_x(\text{CO})_x$ fragments. The W—Se bond length of 2.658 (1) Å is comparable with observed values in $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3(\text{SeCH}_2\text{Ph})$ [2.623 (1) and 2.619 (1) Å for two independent molecules (Eikens, Kienitz, Jones & Thöne, 1994)] and $(\eta^7\text{-C}_7\text{H}_7)(\text{CO})_2\text{W}(\text{SePh})$ [2.588 (2) Å (Rettenmaier, Weidenhammer & Ziegler, 1981)].

Experimental

Orange crystals of the title compound were obtained by layering a dichloromethane solution with diethyl ether.

Crystal data

$[\text{W}(\text{C}_5\text{H}_5)(\text{C}_{18}\text{H}_{15}\text{PSe})\text{(CO)}_3](\text{ClO}_4)$
 $M_r = 773.65$
 Monoclinic
 $P2_1/n$

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 61 reflections
 $\theta = 4.0\text{--}12.5^\circ$

$a = 10.6262(10)$ Å
 $b = 18.101(2)$ Å
 $c = 14.1962(14)$ Å
 $\beta = 107.376(8)^\circ$
 $V = 2606.0(4)$ Å³
 $Z = 4$
 $D_x = 1.972$ Mg m⁻³
 D_m not measured

$\mu = 6.038$ mm⁻¹
 $T = 173(2)$ K
 Prism
 $0.36 \times 0.32 \times 0.20$ mm
 Orange

Data collection

Siemens P4 diffractometer
 ω scans
 Absorption correction:
 ψ scans (XEMP; Nicolet, 1987)
 $T_{\min} = 0.66$, $T_{\max} = 0.92$
 4993 measured reflections
 4555 independent reflections
 3435 observed reflections
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0264$
 $\theta_{\max} = 25.0^\circ$
 $h = -12 \rightarrow 12$
 $k = -21 \rightarrow 1$
 $l = -16 \rightarrow 0$
 3 standard reflections monitored every 247 reflections
 intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0275$
 $wR(F^2) = 0.0560$
 $S = 0.905$
 4554 reflections
 334 parameters
 H atoms refined using a riding model
 $w = 1/[\sigma^2(F_o^2) + (0.0275P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.812$ e Å⁻³
 $\Delta\rho_{\min} = -1.095$ 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 (Å²)

	x	y	z	U_{eq}
W1	0.01576 (2)	0.066638 (11)	0.21876 (2)	0.01727 (6)
Se1	0.27267 (5)	0.03773 (3)	0.28051 (4)	0.02132 (13)
P	0.38984 (13)	0.13675 (7)	0.27591 (10)	0.0166 (3)
Cl	0.7095 (2)	-0.12650 (8)	0.32729 (12)	0.0430 (4)
O11	0.6340 (4)	-0.0730 (2)	0.2607 (3)	0.0494 (12)
O12	0.8420 (4)	-0.1035 (3)	0.3688 (4)	0.0576 (14)
O13	0.7036 (7)	-0.1932 (3)	0.2790 (6)	0.152 (4)
O14	0.6550 (6)	-0.1312 (5)	0.4078 (5)	0.132 (3)
C1	-0.1271 (6)	0.0459 (3)	0.0962 (5)	0.0326 (14)
O1	-0.2112 (5)	0.0342 (2)	0.0251 (3)	0.0564 (14)
C2	0.0239 (6)	-0.0443 (3)	0.2029 (4)	0.0307 (14)
O2	0.0177 (4)	-0.1062 (2)	0.1972 (3)	0.0404 (11)
C3	0.0672 (5)	0.1180 (3)	0.1108 (4)	0.0267 (13)
O3	0.0880 (4)	0.1477 (2)	0.0459 (3)	0.0423 (11)
C11	-0.0256 (5)	0.0559 (3)	0.3709 (4)	0.0285 (13)
C12	0.0567 (5)	0.1187 (3)	0.3803 (4)	0.0270 (12)
C13	-0.0091 (5)	0.1718 (3)	0.3099 (4)	0.0242 (12)
C14	-0.1337 (5)	0.1427 (3)	0.2582 (4)	0.0284 (13)
C15	-0.1450 (5)	0.0714 (3)	0.2953 (4)	0.0283 (12)
C111	0.5431 (5)	0.1293 (3)	0.3728 (4)	0.0183 (11)
C112	0.5912 (5)	0.0612 (3)	0.4146 (4)	0.0251 (12)
C113	0.7154 (5)	0.0586 (3)	0.4852 (4)	0.0314 (13)
C114	0.7411 (5)	0.1883 (3)	0.4709 (4)	0.0309 (13)
C115	0.7884 (5)	0.1209 (4)	0.5129 (4)	0.0338 (14)
C116	0.6199 (5)	0.1930 (3)	0.4022 (4)	0.0251 (12)
C121	0.4306 (5)	0.1458 (3)	0.1607 (4)	0.0197 (11)
C122	0.3870 (6)	0.0941 (3)	0.0881 (4)	0.0338 (14)
C123	0.4137 (6)	0.1027 (4)	-0.0012 (4)	0.041 (2)
C124	0.4851 (5)	0.1620 (3)	-0.0158 (4)	0.0336 (14)
C125	0.5322 (5)	0.2122 (3)	0.0580 (4)	0.0266 (12)

C126	0.5049 (5)	0.2056 (3)	0.1468 (4)	0.0244 (12)
C131	0.3134 (5)	0.2209 (3)	0.2958 (4)	0.0183 (11)
C132	0.2435 (5)	0.2653 (3)	0.2177 (4)	0.0208 (11)
C133	0.1802 (5)	0.3284 (3)	0.2339 (4)	0.0287 (13)
C134	0.1904 (5)	0.3485 (3)	0.3306 (5)	0.0310 (13)
C135	0.2592 (5)	0.3052 (3)	0.4092 (4)	0.0246 (12)
C136	0.3195 (5)	0.2413 (3)	0.3923 (4)	0.0216 (11)

Table 2. Selected geometric parameters (Å, °)

W1—C1	1.974 (6)	W1—Se1	2.6581 (6)
W1—C3	2.003 (6)	Se1—P	2.1944 (14)
W1—C2	2.026 (6)	P—C131	1.789 (5)
W1—C15	2.284 (5)	P—C111	1.796 (5)
W1—C14	2.293 (5)	P—C121	1.821 (5)
W1—C11	2.338 (5)	C1—O1	1.150 (7)
W1—C13	2.361 (5)	C2—O2	1.124 (6)
W1—C12	2.395 (5)	C3—O3	1.143 (6)
C1—W1—C3	74.2 (2)	C111—P—C121	106.9 (2)
C1—W1—C2	76.2 (2)	C131—P—Se1	113.8 (2)
C3—W1—C2	110.2 (2)	C111—P—Se1	108.0 (2)
C1—W1—Se1	134.2 (2)	C121—P—Se1	112.9 (2)
C3—W1—Se1	81.7 (2)	O1—C1—W1	179.3 (5)
C2—W1—Se1	76.6 (2)	O2—C2—W1	173.2 (5)
C15—W1—Se1	133.72 (14)	O3—C3—W1	175.6 (5)
C14—W1—Se1	139.06 (13)	C112—C111—P	121.6 (4)
C11—W1—Se1	97.86 (13)	C116—C111—P	118.8 (4)
C13—W1—Se1	104.48 (13)	C122—C121—P	119.9 (4)
C12—W1—Se1	83.50 (13)	C126—C121—P	119.7 (4)
P—Se1—W1	111.43 (4)	C132—C131—P	121.7 (4)
C131—P—C111	107.0 (2)	C136—C131—P	119.2 (4)
C131—P—C121	107.9 (2)		

Data collection: XSCANS (Siemens, 1994a). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP (Siemens, 1994b). Software used to prepare material for publication: SHELXL93.

We thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauff for technical assistance.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1204). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CHI 2HU, England.

References

- Burger, K., Ottlinger, A., Frank, A. & Schubert, U. (1978). *Angew. Chem.* **90**, 824–825.
- Codding, P. W. & Kerr, K. A. (1979). *Acta Cryst.* **B35**, 1261–1263.
- Colton, R., Hoskins, B. F. & Panagiotidou, P. (1987). *Aust. J. Chem.* **40**, 1909–1912.
- Eikens, W., Kienitz, C., Jones, P. G. & Thöne, C. (1994). *J. Chem. Soc. Dalton Trans.* pp. 3329–3330.
- Glasser, L. S. D., Ingram, L., King, M. G. & McQuillan, G. P. (1969). *J. Chem. Soc. A*, pp. 2501–2504.
- Jones, P. G. & Thöne, C. (1991a). *Inorg. Chim. Acta*, **181**, 291–294.
- Jones, P. G. & Thöne, C. (1991b). *Chem. Ztg.* **115**, 366–367.
- Jones, P. G. & Thöne, C. (1994). *Z. Kristallogr.* **209**, 83–84.
- Jones, P. G., Kienitz, C. & Thöne, C. (1994). *Z. Kristallogr.* **209**, 80–81.
- Nicolet (1987). *Manuals to X-ray Program System*. Nicolet Analytical X-ray Instruments, Madison, USA.
- Pinchuk, V. A., Müller, C., Thönnessen, H., Shermolovich, Y., Jones, P. G. & Schmutzler, R. (1995). *Chem. Ber.* Submitted.

- Rettenmaier, A., Weidenhammer, K. & Ziegler, M. L. (1981). *Z. Anorg. Allg. Chem.* **473**, 91–100.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1994a). *XSCANS*. Version 2.1. Siemens Analytical X-ray Instruments, Madison, USA.
- Siemens (1994b). *XP. Molecular Graphics Program*. Siemens Analytical X-ray Instruments, Madison, USA.

Acta Cryst. (1996). **C52**, 1086–1089

[(R)-1,2-Bis(allyloxycarbonyl)ethyl]bis(dimethylglyoximato-N,N')[(R)-1-phenylethylamine]cobalt(III)

HIROYUKI SATO,^a YOSHII SAKAI,^a YUJI OHASHI,^{a*}
YOSHIFUSA ARAI^b AND YOSHIKI OHGO^b

^aDepartment of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan, and ^bNiigata College of Pharmacy, Kamishin-ei-cho, Niigata 950-21, Japan. E-mail: yohashi@chem.titech.ac.jp

(Received 16 May 1995; accepted 17 October 1995)

Abstract

A new bis(dimethylglyoximato)cobalt(III) complex with a bulky chiral alkyl group bonded to the Co atom has been prepared, [Co(C₄H₇N₂O₂)₂(C₁₀H₁₃O₄)(C₈H₁₁N)]. The crystal was irradiated with a xenon lamp. Racemization of the crystalline state was not observed for the crystal since the reaction cavity for the chiral alkyl group appears to be too small.

Comment

In a series of studies of crystalline-state racemization in bis(dimethylglyoximato)cobalt(III) (cobaloxime) complexes by X-ray or visible-light exposure, three chiral reactive groups, namely, 1-cyanoethyl [ce; –CH(CH₃)CN] (Ohashi, 1988), 1-methoxycarbonyl-ethyl [mce; –CH(CH₃)COOCH₃] (Kurihara, Ohashi, Sasada & Ohgo, 1983; Kurihara, Uchida, Ohashi, Sasada & Ohgo, 1984) and 1,2-dimethoxycarbonyl-ethyl [dmce; –CH(COOCH₃)CH₂COOCH₃] (Sakai *et al.*, 1993; Ohashi *et al.*, 1995), have been found to be racemized with retention of the single-crystal form. The 1,2-diethoxycarbonyl-ethyl group [dece; –CH(COOC₂H₅)CH₂COOC₂H₅] (Yamada *et al.*, 1995), however, did not exhibit crystalline-state racemization. Recently, several cobaloxime complexes having a bulkier chiral group, *i.e.* 1,2-diallyloxycarbonyl-ethyl [dace; –CH(COOCH₂CH=CH₂)CH₂COOCH₂-CH=CH₂], have been prepared. Since well formed