C1—Cr1—C2	93.74 (8)	O103—Na1—O106	64.04 (4)
C1—Cr1—C3	94.71 (8)	O103—Na1—O112	154.97 (4)
C1—Cr1—C4	99.02 (8)	O103—Na1—O120	106.96 (5)
C1—Cr1—C5	94.35 (7)	O103—Na1—O123	101.18 (4)
C1—Cr1—Cr1$^{\text{i}}$	176.10 (5)	O106—Na1—N109	59.25 (5)
C2—Cr1—C4	166.89 (7)	N109—Na1—N100	178.80 (5)
C2—Cr1—Cr1$^{\text{i}}$	82.36 (6)	O112—Na1—O106	94.67 (4)
C3—Cr1—C2	91.74 (9)	O112—Na1—N109	58.98 (5)
C3—Cr1—C4	90.22 (8)	O115—Na1—N100	65.97 (5)
C3—Cr1—Cr1$^{\text{i}}$	85.57 (6)	O115—Na1—O103	102.45 (4)
C4—Cr1—Cr1$^{\text{i}}$	84.87 (6)	O115—Na1—O106	95.74 (4)
C5—Cr1—C2	91.81 (7)	O115—Na1—O112	64.89 (4)
C5—Cr1—C3	170.03 (7)	O115—Na1—O120	101.71 (4)
C5—Cr1—C4	84.26 (7)	O115—Na1—O123	155.46 (5)
C5—Cr1—Cr1$^{\text{i}}$	85.67 (5)	O120—Na1—N100	64.75 (4)
O1—C1—Cr1	178.4 (2)	O120—Na1—O106	161.90 (4)
O2—C2—Cr1	178.4 (2)	O120—Na1—O112	97.03 (4)
O3—C3—Cr1	178.8 (2)	O120—Na1—O123	64.76 (4)
O4—C4—Cr1	176.9 (2)	O123—Na1—N100	119.52 (5)
O5—C5—Cr1	175.46 (14)	O123—Na1—O106	100.48 (4)
N100—Na1—O106	119.57 (4)	O123—Na1—N109	61.03 (4)
N100—Na1—O112	121.72 (5)	O123—Na1—O112	95.34 (4)
O103—Na1—N100	65.12 (4)		

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

Crystal data were collected on a single crystal sealed under dry nitrogen in a 0.2 mm Lindemann glass capillary. Data were collected in two stages: (*a*) 433 exposures (5 min per exposure) were obtained at 50 mm with $40 \leq \varphi \leq 169.9°$ and with the crystal oscillated through 0.3° in φ; (*b*) 160 exposures (3 min per exposure) were obtained at 125 mm with $40 \leq \varphi \leq 200°$ and with the crystal oscillated through 1° in φ. The two data sets were merged and the final data set contained 92% of the calculated number of unique reflections. Computations were carried out on a Silicon Graphics Model 4600 PC workstation. During refinement, 92 reflections were either omitted if $F^2 < 0$ or flagged for potential systematic errors. H-atom positions were calculated and C—H was fixed to 0.96 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the parent atom.

Data collection: *IPDS* (Stoe, 1995). Cell refinement: *IPDS*. Data reduction: *IPDS*. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BR1160). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bisphenylbis[tetracarbonyl(hydrido)osmio]germane, $Ph_2Ge[Os(CO)_4H]_2$

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Abstract

The title compound, octacarbonyl-1κ^4C,2κ^4C-dihydrido-1κH,2κH-bis(phenyl-3κC)germaniumdiosmium(2 *Ge*—*Os*), $[Os_2(H)_2(CO)_8\{Ge(C_6H_5)_2\}]$, is the first cluster containing a single Os—*E*—Os (*E* = Ge, Sn or Pb) chain to be structurally characterized. The molecule possesses approximate C_2 symmetry. The Os—Ge—Os metal chain is bent and the Os—Ge bonds [2.599 (2) and 2.614 (2) Å] are the longest yet known.

Comment

The title compound, (I), was obtained in low yield as a by-product from the preparation of $[Ph_2SnOs(CO)_4]_2$ by the reaction of equimolar amounts of Ph_2GeCl_2 and $Na_2Os(CO)_4$. We believe that its formation resulted from partial hydrolysis of the very moisture-sensitive $Na_2Os(CO)_4$ to $NaHOs(CO)_4$, which subsequently attacked the Ph_2GeCl_2.

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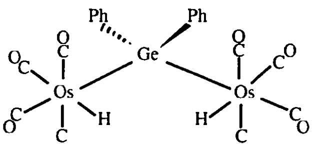

(I)

The title compound is the first example of an Os—*E*—Os (*E* = Ge, Sn or Pb) chain to be structurally characterized (Fig. 1); the only other known Os—*E*—Os chain is cationic $Cl_2Sn[Os(Cp)_2]_2^{2+}$, which was characterized spectroscopically (Watanabe & Sano, 1990). Similar Fe analogues have, however, been known for some time and at least one has been structurally characterized, namely, $Cl_2Ge[Fe(CO)_2Cp]_2$ (Bush & Woodward, 1967).

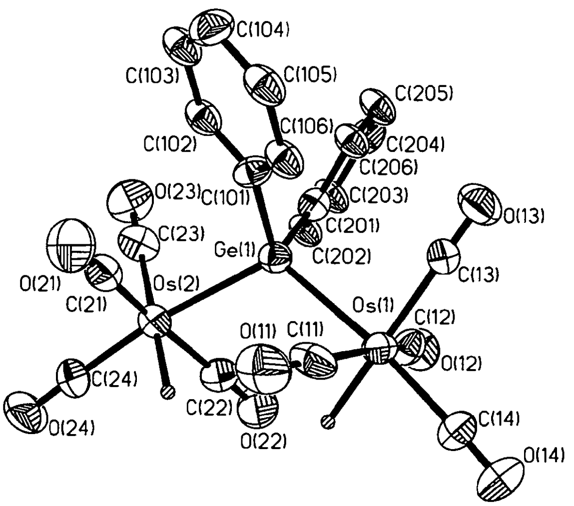

Fig. 1. *ORTEP*II (Johnson, 1976) diagram (30% probability displacement ellipsoids) showing the atomic numbering scheme for $Ph_2Ge[Os(CO)_4H]_2$.

Although there is no crystallographically imposed symmetry, the molecule does possess an approximate C_2 axis passing through the Ge atom and the midpoint of the Os···Os vector. Although the hydrides were not located directly, their presence was indicated by a −8.12 p.p.m. signal in the ^1H NMR spectrum, which is consistent with a terminal OsH group. Based on steric considerations, they were placed in calculated positions *trans* to a CO ligand on each of the Os atoms. The hydrides are *cis* with respect to the Ge atom and point towards one another. The location of the hydride ligands on the inside of the bent metal chain may be attributed to the smaller steric bulk of the hydrides compared with the carbonyl ligands. This reduced steric bulk of the hydrides may also have allowed the bending of the carbonyl groups that are *cis* to the H and Ge atoms towards the hydrides, and the smaller Os—Ge—Os angle of 114.41 (6)° compared with a value of 128 (1)° for the corresponding angle in $Cl_2Ge[Fe(CO)_2Cp]_2$. The larger than tetrahedral Os—Ge—Os angle is also in accord with the trend found in tin transition metal compounds (Zubieta & Zuckerman, 1978).

The Os—Ge bond lengths in the title compound [2.599 (2) and 2.614 (2) Å] are longer than those found in any other structurally characterized clusters containing germanium and osmium (Leong, Pomeroy & Einstein, 1995). The difference in the two Os—Ge bond lengths is statistically significant, but can probably be attributed to crystal-packing forces.

Experimental

An equimolar amount of Ph_2GeCl_2 was added to $Na_2Os(CO)_4$, prepared from the sodium reduction of $Os_3(CO)_{12}$ in liquid ammonia (George, Knox & Stone, 1973), followed by tetrahydrofuran (pre-chilled at 223 K). The mixture was allowed to warm slowly to room temperature overnight, with stirring. The solvent was removed *in vacuo* and the residue extracted with hexane. The extract was then filtered through a short column of silica, concentrated and cooled to yield small amounts of the title compound as pale yellow crystals.

Crystal data

$[Os_2(H)_2(CO)_8\{Ge(C_6H_5)_2\}]$
$M_r = 833.30$
Monoclinic
$C2/c$
$a = 33.775\ (6)$ Å
$b = 9.5143\ (11)$ Å
$c = 14.987\ (3)$ Å
$\beta = 105.433\ (14)°$
$V = 4642.4\ (14)$ Å^3
$Z = 8$
$D_x = 2.385$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 15–17°$
$\mu = 12.24$ mm^{-1}
$T = 294$ K
Rectangular prism
0.30 × 0.27 × 0.18 mm
Pale yellow

Data collection

Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian by integration from crystal shape (Busing & Levy, 1957)
$T_{\min} = 0.1321$, $T_{\max} = 0.2593$
3227 measured reflections
2995 independent reflections

2340 observed reflections $[I_{\rm net} > 2.5\sigma(I_{\rm net})]$
$R_{\rm int} = 0.023$
$\theta_{\max} = 22.5°$
$h = -36 \rightarrow 34$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 16$
2 standard reflections
frequency: 60 min
intensity decay: 50%

Refinement

Refinement on F
$R = 0.045$
$wR = 0.055$
$S = 3.0$
2340 reflections
215 parameters
H atoms: see below
$w = 1/[0.0001|F_o|^2 + \sigma^2(F_o)]$
$(\Delta/\sigma)_{\max} = 0.11$
$\Delta\rho_{\max} = 1.6\ (2)$ e Å^{-3}
$\Delta\rho_{\min} = -1.0\ (2)$ e Å^{-3}

Extinction correction: Larson (1970)
Extinction coefficient: 0.16 (3)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	U_{eq}
Os(1)	0.58045 (2)	0.04319 (6)	0.16885 (4)	0.0628
Os(2)	0.58275 (2)	0.43598 (7)	0.32288 (5)	0.0736
Ge(1)	0.62469 (4)	0.2281 (1)	0.27946 (9)	0.0584
O(11)	0.5489 (4)	−0.014 (2)	0.3394 (9)	0.1091
O(12)	0.5988 (4)	0.222 (1)	0.0145 (7)	0.0947
O(13)	0.6570 (4)	−0.151 (1)	0.2056 (8)	0.0949
O(14)	0.5206 (4)	−0.156 (1)	0.0364 (9)	0.1070
O(21)	0.6014 (4)	0.306 (2)	0.5174 (9)	0.1203
O(22)	0.5519 (4)	0.467 (1)	0.1110 (9)	0.1121
O(23)	0.6611 (4)	0.625 (1)	0.364 (1)	0.1136
O(24)	0.5225 (4)	0.654 (1)	0.363 (1)	0.1211
C(11)	0.5606 (4)	−0.006 (2)	0.276 (1)	0.0782
C(12)	0.5933 (5)	0.151 (2)	0.071 (1)	0.0711
C(13)	0.6295 (5)	−0.083 (2)	0.193 (1)	0.0708
C(14)	0.5422 (5)	−0.086 (2)	0.083 (1)	0.0852
C(21)	0.5956 (5)	0.353 (2)	0.447 (1)	0.0825
C(22)	0.5642 (5)	0.459 (2)	0.191 (1)	0.0897
C(23)	0.6324 (5)	0.557 (2)	0.348 (1)	0.0857
C(24)	0.5453 (6)	0.571 (2)	0.349 (1)	0.0944
C(101)	0.6585 (2)	0.1391 (9)	0.3950 (5)	0.0584
C(102)	0.6864 (3)	0.2276 (7)	0.4548 (6)	0.0626
C(103)	0.7129 (2)	0.1756 (9)	0.5373 (5)	0.0657
C(104)	0.7115 (3)	0.035 (1)	0.5600 (5)	0.0773
C(105)	0.6836 (3)	−0.0536 (7)	0.5003 (6)	0.0657
C(106)	0.6571 (2)	−0.0015 (8)	0.4178 (5)	0.0626
C(201)	0.6684 (2)	0.2987 (8)	0.2250 (6)	0.0600
C(202)	0.6625 (2)	0.4199 (8)	0.1695 (6)	0.0627
C(203)	0.6941 (3)	0.4666 (8)	0.1309 (6)	0.0679
C(204)	0.7317 (2)	0.392 (1)	0.1477 (7)	0.0935
C(205)	0.7376 (2)	0.271 (1)	0.2032 (7)	0.0679
C(206)	0.7060 (3)	0.2242 (7)	0.2418 (6)	0.0627

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

Os(1)—Ge(1)	2.599 (2)	Ge(1)—C(101)	1.992 (6)
Os(1)—C(11)	1.95 (2)	Ge(1)—C(201)	1.986 (6)
Os(1)—C(12)	1.94 (2)	O(11)—C(11)	1.13 (2)
Os(1)—C(13)	2.00 (2)	O(12)—C(12)	1.13 (1)
Os(1)—C(14)	1.98 (2)	O(13)—C(13)	1.11 (2)
Os(2)—Ge(1)	2.614 (2)	O(14)—C(14)	1.10 (2)
Os(2)—C(21)	1.97 (2)	O(21)—C(21)	1.11 (2)
Os(2)—C(22)	1.93 (2)	O(22)—C(22)	1.16 (2)
Os(2)—C(23)	1.99 (2)	O(23)—C(23)	1.14 (2)
Os(2)—C(24)	1.92 (2)	O(24)—C(24)	1.16 (2)
Os(1)—Ge(1)—Os(2)	114.41 (6)	Os(2)—C(21)—O(21)	177.5 (16)
Os(1)—C(11)—O(11)	170.2 (17)	Os(2)—C(22)—O(22)	176.1 (18)
Os(1)—C(12)—O(12)	174.9 (14)	Os(2)—C(23)—O(23)	178.2 (17)
Os(1)—C(13)—O(13)	178.7 (15)	Os(2)—C(24)—O(24)	178.5 (19)
Os(1)—C(14)—O(14)	178.8 (16)		

The phenyl C atoms were regularized, with C—C bond lengths of 1.39 Å, and the phenyl H atoms were placed in calculated positions, with C—H bond lengths of 1.0 Å. The phenyl rings were refined as rigid groups pivoted about dummy atoms placed at the centroids. Equivalent phenyl C atoms were given the same displacement parameters and their shifts made equivalent, giving four sets of U_{ij} per phenyl ring. The metal hydrides were also placed in calculated positions, at 1.66 Å from their attached Os atoms and *trans* to a CO group.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX DATRD*2 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *NRCVAX TABLES*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1150). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Chloro-Bridged Osmium Clusters

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Abstract

The molecular structure of the chloro-bridged tetraosmium cluster, dodecacarbonyl-1κ^3C,2κ^3C,3κ^3C,4κ^3C-μ-chloro-3:4κ^2Cl-tris-μ-hydrido-1:2κ^2H;1:3κ^2H;2:4κ^2H-tetraosmium(5 *Os*—*Os*), $[Os_4(\mu\text{-}Cl)(\mu\text{-}H)_3(CO)_{12}]$, consists of a 'butterfly' arrangement of Os atoms, just as in the iodo analogue. The chloro bridge in the tetraosmium cluster is symmetric, whereas in the pentaosmium cluster, tetradecacarbonyl-1κ^3C,2κ^2C,3κ^3C,4κ^3C,5κ^3-μ-chloro-2:5κ^2Cl-tris-μ-hydrido-1:2κ^2H;2:3κ^2H;2:4κ^2H-