$a = 10.320\,(4)$ Å
$b = 17.062\,(8)$ Å
$c = 21.803\,(1)$ Å
$\beta = 90.28\,(2)°$
$V = 3839\,(2)$ Å^3
$Z = 4$
$D_x = 1.42$ Mg m^{-3}
D_m not measured

$\mu = 0.53$ mm^{-1}
$T = 293$ K
Parallelepiped
$0.2 \times 0.1 \times 0.1$ mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.71$, $T_{\max} = 0.95$
6454 measured reflections
6164 independent reflections

4722 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.03$
$\theta_{\max} = 25°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 20$
$l = -25 \rightarrow 0$
3 standard reflections frequency: 60 min intensity decay: 1.9%

Refinement

Refinement on F
$R = 0.040$
$wR = 0.049$
$S = 1.065$
4722 reflections
470 parameters
H atoms placed geometrically after each cycle
Weighting scheme: Chebychev polynomial (Carruthers & Watkin, 1979)

$(\Delta/\sigma)_{\max} = 0.318$
$\Delta\rho_{\max} = 0.94$ e Å^{-3}
$\Delta\rho_{\min} = -0.52$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 13.749
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å)*

Ru1—P1	2.3434 (9)	N1—C6	1.129 (6)
Ru1—P2	2.365 (1)	C1—C2	1.436 (7)
Ru1—N1	2.040 (3)	C1—C5	1.399 (7)
Ru1—C1	2.210 (4)	C2—C3	1.416 (7)
Ru1—C2	2.205 (4)	C3—C4	1.409 (7)
Ru1—C3	2.208 (4)	C4—C5	1.419 (7)
Ru1—C4	2.202 (4)	C6—C7	1.450 (9)
Ru1—C5	2.204 (4)		

All non-H atoms refined anisotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *RC*93 (Watkin, Prout & Lilley, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1996). Molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1996). Software used to prepare material for publication: *CRYSTALS*.

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Acta Cryst. (1997). C**53**, 302-305

Nonacarbonyl[μ_3-(1,2-diphenylethyl)-phenylphosphinito]triosmium(2 *Os—Os*)

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Abstract

The reaction of 1,2,3-triphenylphosphirene with $[H_2Os_3(CO)_{10}]$ leads to the title compound, $[Os_3(CO)_9\{(C_6H_5)_3C_2PO\}]$, which displays an open $Os_3(CO)_9$ cluster [Os—Os 2.703 (1) and 2.867 (2) Å, and Os—Os—Os 124.24 (4)°]. This moiety is μ_3,η^3-bonded to a phosphirene ligand with a cleaved P—C bond, PhC—C(Ph)—P. An O atom was incorporated into the molecule resulting in an unusual five-membered metallacycle,

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FR1009). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Os—C—C—P—O, with distances Os—C 2.10 (1), C—C 1.46 (2), C—P 1.76 (1), P—O 1.628 (9) and O—Os 2.136 (9) Å. This ring makes a dihedral angle of 57.3 (2)° with the plane of the metal atoms.

Comment

Three-membered phosphirene rings, (*R*C═C*R*)P*R*, are potentially very useful precursors to a range of organometallic ligands such as acetylenes, phosphine-indenes and various other linked systems (Marinetti, Fischer & Mathey, 1985; Svara, Marinetti & Mathey, 1986; Carmichael, Hitchcock, Nixon, Mathey & Pidcock, 1986). We recently studied the reaction of 1,2,3-triphenylphosphirene, (PhC═CPh)PPh, with $[Ru_3(CO)_{12}]$ (Arce *et al.*, 1995), which was found to produce the complex $[Ru_3(CO)_8(\mu_3\text{-}C_4Ph_6P_2)]$ containing two opened and coupled phosphirene rings. We report here the results of a similar reaction with $[H_2Os_3(CO)_{10}]$, which afforded a different and totally unexpected compound, (I).

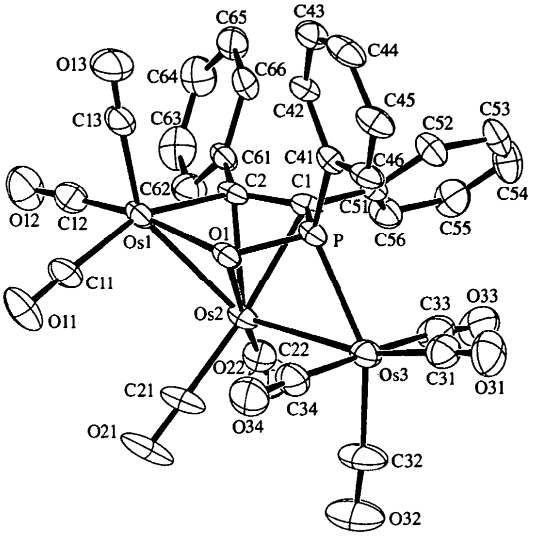
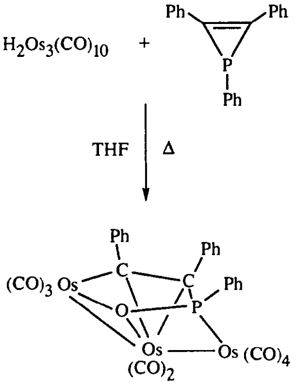


Fig. 1. The molecular structure of the title compound showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.



(I)

The structure analysis of the reaction product showed that the crystals contain discrete molecules of $[Os_3(CO)_9(Ph_3C_2PO)]$ (Fig. 1). The title compound displays an open $Os_3(CO)_9$ cluster μ_3,η^3-bonded to a phosphirene ligand in which one of the P—C bonds was cleaved, as in the Ru complex reaction mentioned above. In this case, however, an O atom (O1) was incorporated into the molecule resulting in an unusual five-membered Os1—C2—C1—P—O1 ring. The source of this atom could be either a carbonyl group, molecular oxygen or moisture. The first possibility is very unlikely due to the stability of the C≡O bond, so that it is probable that the O1 atom comes from a contaminant, presumably moisture. In spite of repeated efforts (see *Experimental*), we were unable to establish and/or eliminate the source of the O atom.

We have no doubt that O1 is a single O atom (not OH). The evidence is both crystallographic (U_{eq} value for O1 is quite sensible as opposed to refinement as C or N) and chemical spectroscopic (the electron count for the cluster is precise); the CPh—CPh—PPh—O ligand acts as an eight-electron donor group for a 50-electron cluster, there are only two Os—Os bonds and no evidence of Os—H in the ^{1}H NMR spectrum.

The Os2—Os3 bond length is within the range of distances observed in other open Os_3 clusters, *e.g.* 2.819 (2)–2.930 (2) Å in $[HOs_3(CO)_9(PC_4H_4Me)(C_6H_4)]$ (Deeming, Powell, Arce, De Sanctis & Manzur, 1991) and 2.813 (1)–2.948 (1) Å in $[Os_3(CO)_9(PhPC_4H_4)]$ (Arce, De Sanctis, Manzur, Deeming & Powell, 1991). On the other hand, the O1 atom bridging the Os1 and Os2 atoms produces a significant shortening of the Os1—Os2 distance. The Os3—P bond length is within the range of distances (*ca* 2.32–2.41 Å) observed for Os—P bonds in tertiary phosphines (Orpen *et al.*, 1989) and similar to an equivalent Ru—P distance [2.337 (1) Å] found in $[Ru_3(CO)_8(\mu_3\text{-}C_4Ph_6P_2)]$ (Arce *et al.*, 1995). The Os2···P non-bonded distance is 2.581 (4) Å. The Os—C bonds to the vinyl moiety which bridges Os1 and Os2 (*i.e.* Os1—C2, Os2—C1 and Os2—C2) have lengths comparable to the equivalent Ru—C bonds of $[Ru_3(CO)_8(\mu_3\text{-}C_4Ph_6P_2)]$, *i.e.* 2.093 (4), 2.316 (4) and 2.217 (4) Å, respectively. In the present structure, however, both π bonds are equal, while in $[Ru_3(CO)_8(\mu_3\text{-}C_4Ph_6P_2)]$, they are significantly asymmetric, probably due to steric distortion. As expected, the Os1—O1 σ bond is significantly shorter than the Os2—O1 π bond.

The P atom lies 0.995 (4) Å from the plane of the metal atoms and displays a distorted tetrahedral environment, with angles in the range 96.9 (6)–126.8 (5)°.

The P—C and P—O distances are within normal ranges (Allen *et al.*, 1987).

The most interesting feature of this compound is the five-membered Os—C—C—P—O metallacycle. To the best of our knowledge, no compound containing a similar ring with any transition metal has been structurally characterized so far. The ring is nearly planar, but is better described as an envelope, with the O1 atom at a distance of 0.324 (9) Å (towards Os2) from the plane of the other four atoms (mean deviation from plane is 0.015 Å). The C51 and C61 atoms are approximately coplanar with that plane [distances to plane are 0.04 (1) and 0.24 (1) Å, respectively], while it makes a dihedral angle of 57.3 (2)° with the Os_3 plane.

Experimental

1,2,3-Triphenylphosphirene, (PhC═CPh)PPh, was prepared according to the method of Lochsmidt, Mathey & Schmidpeter (1986). To a solution of [$H_2Os_3(CO)_{10}$] (0.10 g, 0.12 mmol) in dry THF (40 ml) was added an equimolar amount of triphenylphosphirene (0.34 g, 0.12 mmol) and the resulting solution heated under reflux under nitrogen for 24 h. Removal of the solvent *in vacuo* and TLC separation (SiO_2, *n*-hexane) yielded the title compound (0.011 g; yield 8%) as a yellow solid. Crystals suitable for X-ray analysis were obtained by slow evaporation of a cyclohexane solution. To establish the source of a possible contaminant, and eventually to eliminate it, we repeated the reaction three times, but in all cases we obtained the same results. To avoid molecular oxygen, the nitrogen gas was passed through a trap containing Cr^{2+}/Zn–Hg and to ensure the dryness of the solvents they were distilled over Na wire (using benzophenone as an indicator).

Crystal data

[$Os_3(C_{20}H_{15}OP)(CO)_9$]
$M_r = 1125.01$
Monoclinic
$P2_1/n$
$a = 11.049\ (6)$ Å
$b = 17.638\ (3)$ Å
$c = 15.894\ (2)$ Å
$\beta = 91.12\ (2)°$
$V = 3097\ (1)$ Å^3
$Z = 4$
$D_x = 2.413$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 23.5$–$28.9°$
$\mu = 12.377$ mm^{-1}
$T = 295\ (1)$ K
Prism
0.33 × 0.15 × 0.13 mm
Yellow

Data collection

Rigaku AFC-7*S* diffractometer
ω–2θ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.488$, $T_{\max} = 1.000$
5624 measured reflections
5316 independent reflections

4133 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.0236$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 20$
$l = -18 \rightarrow 18$
3 standard reflections every 150 reflections intensity decay: 18.2%

Refinement

Refinement on F
$R = 0.0454$
$wR = 0.0552$
$S = 3.200$
4133 reflections
403 parameters
Only H-atom U's refined
Weighting scheme based on counting statistics

$(\Delta/\sigma)_{\max} = 0.0007$
$\Delta\rho_{\max} = 1.67$ e Å^{-3}
$\Delta\rho_{\min} = -1.61$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Os1—Os2	2.703 (1)	Os3—P	2.367 (4)
Os1—O1	2.136 (9)	Os3—C31	1.94 (2)
Os1—C2	2.10 (1)	Os3—C32	1.96 (2)
Os1—C11	1.96 (2)	Os3—C33	2.00 (2)
Os1—C12	1.82 (2)	Os3—C34	1.95 (2)
Os1—C13	1.93 (2)	P—O1	1.628 (9)
Os2—Os3	2.867 (2)	P—C1	1.76 (1)
Os2—O1	2.188 (9)	P—C41	1.81 (1)
Os2—C1	2.31 (1)	C1—C2	1.46 (2)
Os2—C2	2.32 (1)	C1—C51	1.50 (2)
Os2—C21	1.87 (2)	C2—C61	1.47 (2)
Os2—C22	1.87 (2)		
Os2—Os1—O1	52.2 (2)	O1—P—C41	105.6 (6)
Os2—Os1—C2	56.0 (4)	C1—P—C41	115.4 (6)
O1—Os1—C2	78.5 (5)	Os1—O1—Os2	77.4 (3)
Os1—Os2—Os3	124.24 (4)	Os1—O1—P	123.7 (5)
Os1—Os2—O1	50.5 (2)	Os2—O1—P	83.7 (4)
Os1—Os2—C1	75.7 (3)	Os2—C1—P	77.3 (4)
Os1—Os2—C2	48.8 (3)	Os2—C1—C2	71.7 (7)
Os3—Os2—O1	74.1 (2)	Os2—C1—C51	126.0 (9)
Os3—Os2—C1	79.3 (3)	P—C1—C2	117.8 (9)
Os3—Os2—C2	115.1 (3)	P—C1—C51	121 (1)
O1—Os2—C1	68.6 (4)	C2—C1—C51	120 (1)
O1—Os2—C2	73.0 (4)	Os1—C2—Os2	75.2 (4)
C1—Os2—C2	36.8 (5)	Os1—C2—C1	119.4 (9)
Os2—Os3—P	58.14 (9)	Os1—C2—C61	119.3 (9)
Os3—P—O1	99.9 (4)	Os2—C2—C1	71.5 (7)
Os3—P—C1	106.7 (5)	Os2—C2—C61	130.8 (9)
Os3—P—C41	126.8 (5)	C1—C2—C61	120 (1)
O1—P—C1	96.9 (6)		

An absorption correction based on ψ-scan data gave unsatisfactory results. Better results were obtained with the *DIFABS* (Walker & Stuart, 1983) procedure. H atoms were placed in calculated positions (C—H 0.96 Å) and assigned fixed coordinates and refined with individual isotropic displacement parameters. The structure contains two symmetry-related solvent accessible voids (0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$) of ≈60 Å^3 each, however, no significant peaks were found there. The 12 largest peaks in the final difference map were near osmium and were interpreted as residual absorption effects.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick. 1990). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: SK1030). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 305–309

Hexakis(dimethylformamide)bis(hexaphenylcyclohexasiloxanehexaolato)hexacopper(II) Dimethylformamide Solvate

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Abstract

The sandwich-like title complex, hexakis(dimethylformamide)-$1\kappa O,2\kappa O,3\kappa O,4\kappa O,5\kappa O,6\kappa O$-bis[2,4,6,8,10,12-hexaphenylsiloxane-2,4,6,8,10,12-hexaolato(6−)-$1{:}2\kappa^2O^1,2{:}3\kappa^2O^2,3{:}4\kappa^2O^3,4{:}5\kappa^2O^4,5{:}6\kappa^2O^5,1{:}6\kappa^2O^6$]-hexacopper(II) tetrakis(dimethylformamide) solvate, $[Cu_6(C_3H_7NO)_6\{(C_6H_5)_6O_{12}Si_6\}_2].4C_3H_7NO$, is comprised of two regular crown-shaped macrocyclic hexadentate organosiloxanolate ligands chelating a flat Cu_6 hexagon, as in the ethanol-solvated analogue investigated previously. The title complex has a more distorted shape than the trigonal ethanol-solvated analogue, being slightly side-oblated, but still contains a large empty inner channel accessible by small molecules (the diameter of the free cross-section being about 2.5 Å). Each Cu^{II} ion has a square-pyramidal coordination comprised of four basal siloxanolate O atoms and an apical dimethylformamide (DMFA) molecule (coordinated through its carbonyl group). The average bond lengths are Cu—O(Si) 1.964 (11) and Cu—O(DMFA) 2.215 (10) Å. The structure contains four additional DMFA molecules per complex unit, linked by weak C—H···O hydrogen bonds. Unexpectedly, the C=O bond length is longer [1.248 (10) and 1.255 (9) Å] in the uncoordinated DMFA molecules than in the coordinated molecules [1.214–1.227 (7) Å].

Comment

Recently, a new class of polynuclear metal complexes has been obtained (involving alkaline metals, Mn, Co, Ni and other bivalent transition metals, Cu and trivalent lanthanides) with polydentate regular macrocyclic organosiloxanolate $[\text{-}R\text{Si(O}^-\text{)O-}]_n$ ligands (n = 6, 8 or 12), which are known as polymetalloorganosiloxanolates (PMOS) and have been structurally characterized by Struchkov & Lindeman (1995). The size and structure of the organocyclosiloxanolate ligands formed seem to be dependent mainly on the coordination characteristics (size, charge and coordination number) of the metal. The Cu^{II} complexes are of special interest since at least two quite different structural types have been obtained using different reaction conditions, *i.e.* sandwich-like complexes, such as $[Cu_6\{(C_6H_5)_6O_{12}Si_6\}(EtOH)_6]$ [(1); Igonin *et al.*, 1992] or $K_2[K_2Cu_4\{(C_2H_5)_6O_{12}Si_6\}].4n$-BuOH [(2); Igonin *et al.*, 1993], and globular-like complexes, such as $[Na_4Cu_4\{(C_6H_5)_{12}O_{24}Si_{12}\}].8n$-BuOH, (3), and $K_4[Cu_4(O_{24}Si_{12}Vi_{12})].6n$-BuOH [(4); Igonin *et al.*, 1991].

Complex (1) is rather unique as a result of its large empty inner channel and square-pyramidal coordination of the Cu atoms (by four siloxanolate groups and an axial solvent hydroxy group); other complexes have more compact structures and contain square-planar-coordinated Cu ions without the additional coordination by solvent molecules. To obtain additional evidence on the stability and reproducibility of such an open structure [in related PMOS compounds based on bivalent *d*-group metals or trivalent lanthanides, the central cavity is occupied by an additional small anion (Cl^-, OH^- or O^{2-}) (Struchkov & Lindeman, 1995)], a close ana-

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