metal-organic compounds

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Hydrido-sulfido-bridged triangular Os₃ cluster compounds with different phosphine ligand substitution patterns

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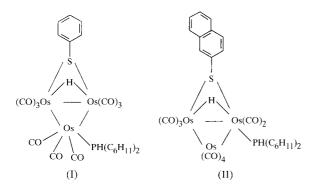
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In the course of our studies of trinuclear osmium cluster complexes with bridging sulfido and hydrido ligands, the new compounds $Os_3(\mu-H)(\mu-SR)(CO)_9(PHCy_2)$ (Cy = cyclohexyl) with R = phenyl, (I) (nonacarbonyl-1 $\kappa^3C, 2\kappa^3C, 3\kappa^3C$ -dicyclohexylphosphine- $3\kappa P$ - μ -hydrido-1: $2\kappa^2H$ - μ -phenylthio-1: $2\kappa^2S$ -triangulo-triosmium), [Os₃H(C₆H₅S)(C₁₂H₂₃P)(CO)₉], and R = naphthyl, (II) [nonacarbonyl-1 $\kappa^3C, 2\kappa^2C, 3\kappa^4C$ -dicyclohexylphosphine- $2\kappa P$ - μ -hydrido-1: $2\kappa^2H$ - μ -(2-naphthylthio)-1: $2\kappa^2S$ -triangulo-triosmium], [Os₃H(C₁₀H₇S)(C₁₂H₂₃P)(CO)₉], were prepared. We report on these two phosphine-substituted complexes, which exhibit perceptible changes of the Os–Os bond parameters due to the ligand-substitution pattern.

Comment

Structure reports on triangular $Os_3(\mu-H)(\mu-SR)(CO)_{10-n}L_n$ (n = 0 or 1) compounds show rather differing patterns of Os – Os distances, and the positions of the μ -H atoms, though confirmed by spectroscopic methods, have not been determined (Adams & Dawoodi, 1981; Brodie *et al.*, 1983; Ditzel *et al.*, 1987; Holden *et al.*, 1983; Monari *et al.*, 1996). We present here the structures of two similar compounds, (I) and (II), together with details of the μ -H atoms.



The molecular structure of (I) (Fig. 1) depicts a triangular arrangement of the three Os atoms. Of these, Os2 and Os3 each have three terminal carbonyl groups and common bridging μ -H and μ -S atoms as ligands. The CO groups show an

ecliptic arrangement, with torsion angles C5-Os2-Os3-C7-0.2 (5), C6-Os2-Os3-C8 -2.2 (7) and C4-Os2-Os3-C9-6.4 (6)°. The third metal atom, Os1, has two axially and one equatorially attached CO group, as well as an equatorially positioned PHCy₂ ligand. Considering two Os-Os bonds for each metal atom, Os1 thus achieves a sixfold distorted octahedral coordination, whereas the two bridged atoms (Os2 and Os3) have sevenfold coordination.

The Os₂ μ -H and Os₂ μ -S planes form a dihedral angle of 52.0 (1)°, and the dihedral angles with the central Os₃ ring are 73.7 (1)° for the Os₂ μ -S plane and 125.7 (1)° for Os₂ μ -H. Two edges, Os1–Os3 of 2.8678 (7) and Os2–Os3 of 2.8674 (7) Å, are equal and clearly longer than the Os1–Os2 edge of 2.8382 (7) Å. One of the long edges is bridged by the two μ -H and μ -S ligands, and the short Os–Os edge has the PHCy₂ ligand in the *trans* position.

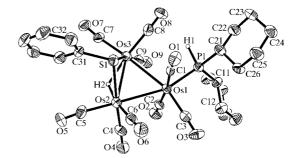


Figure 1

The molecular structure of (I) showing 50% probability displacement ellipsoids. Phenyl and cyclohexyl H atoms have been omitted for clarity.

The sulfido bridge is symmetric, with equal Os-S bond lengths of 2.412 (3) and 2.413 (3) Å, and compares well with that known from the above-mentioned related Os₃ clusters. The S-C_{phenyl} distance of 1.803 (10) Å is consistent with a single bond and the plane of the phenyl ring is nearly perpendicular to the Os₃ plane at an angle of 85.0 (1)°.

The molecular structure of (II) (Fig. 2) is closely related to that of (I) but with substitution of a naphthyl group rather than a phenyl group on the μ -S ligand. The deciding difference, however, is the position of the PHCy₂ group, which is pseudo-*trans* to the bridged Os–Os bond and is attached to Os2. The Os2–P bond length of 2.345 (2) Å is equal to that for (I) [2.342 (3) Å] and the coordination geometry of (II) is almost the same as for (I), with torsion angles C5–Os2–Os3–C7 0.1 (4), C6–Os2–Os3–C8 1.3 (4) and P1–Os2–Os3–C9 9.9 (4)°.

The dihedral angle between the $Os_2\mu$ -H and $Os_2\mu$ -S planes is 47.3 (1)° and the dihedral angles between the Os_3 ring and $Os_2\mu$ -S and $Os_2\mu$ -H planes are 77.1 (1) and 124.4 (1)°, respectively. The Os-S bond lengths of 2.423 (2) and 2.434 (2) Å differ only slightly and S- $C_{naphthyl}$ is 1.798 (8) Å. However, the Os₃ ring geometry has changed, obviously due to the different substitution pattern of the metal atoms. In (II), there are two nearly equal but short bond lengths, Os1-Os3 2.8544 (6) Å and Os2-Os3 2.8585 (5) Å, and one long Os1-Os2 edge of 2.8928 (5) Å. This latter edge is now *cis* to the PHCy₂ ligand at Os2.

 $D_x = 2.390 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation Cell parameters from 23

reflections

 $\begin{array}{l} \theta = 14.45\text{--}37.96^{\circ} \\ \mu = 12.263 \ \mathrm{mm^{-1}} \end{array}$

T = 203 (2) K

Block, yellow

 $\begin{aligned} R_{\rm int} &= 0.047\\ \theta_{\rm max} &= 27.5^\circ \end{aligned}$

 $h = -27 \rightarrow 1$

 $k = -1 \rightarrow 11$

 $l = -43 \rightarrow 43$

3 standard reflections

every 397 reflections

intensity decay: 5%

 $(\Delta/\sigma)_{\rm max} = 0.001$

 $\Delta \rho_{\rm max} = 0.91 \ {\rm e} \ {\rm \AA}^{-3}$

 $\Delta \rho_{\rm min} = -0.98 \ {\rm e} \ {\rm \AA}^{-3}$

 $w = 1/[\sigma^2(F_o^2) + (0.0145P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

 $0.27 \times 0.14 \times 0.08 \text{ mm}$

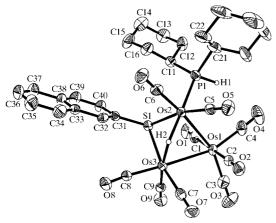


Figure 2

The molecular structure of (II) showing 50% probability displacement ellipsoids. Naphthyl and cyclohexyl H atoms have been omitted for clarity.

The μ -H atoms of (I) and (II) have been located from difference Fourier maps and refined. Both lie above the Os₃ planes if the μ -S atoms are considered to lie below these planes. The mean Os-H bond lengths are 1.86 (8) Å for (I) and 1.70 (12) Å for (II).

The coordination geometry of (II) is just the same as for $Os_3(\mu-H)(\mu-SPh)(CO)_9(PEt_3)$, (III) (Ditzel *et al.*, 1987), but in this complex, there are two long [2.883 (1) and 2.901 (1) Å] and one short [2.862 (1) Å] Os—Os edge. The short edge is between the two Os atoms which are not coordinated by the phosphine group and this ligand is pseudo-*trans* to the bridged Os—Os edge. The same order of long and short Os—Os edges [2.873 (1), 2.880 (1) and 2.855 (1) Å] is valid for the compound $Os_3(\mu-H)(\mu-SCH_2CH=CH_2)(CO)_9(PPh_3)$, (IV) (Adams & Pompeo, 1992), but here the phosphine ligand is *cis* to the μ -H– μ -S bridged Os—Os edge.

In summary, these four phosphine-substituted cluster complexes each have in common two equal and one significantly different Os—Os edge. The accompanying bond-length differences range from 0.015 Å for (IV) to 0.032 Å for (II), taking the reported s.u.'s into account. There is, however, no clear conjunction between the substitution pattern and the sequence of Os—Os bonds. Related unsubstituted Os₃ carbonyl compounds exhibit almost equal bond lengths for all three Os—Os edges, *e.g.* Os₃(μ -H)[μ -SC(H)N-p-C₆H₄F]-(CO)₁₀ (Adams & Dawoodi, 1981) with a bond difference, Δ , of 0.003 Å, Os₃(μ -H)(μ -SC=NCH₂CH₂S)(CO)₁₀ (Δ = 0.002 Å; Brodie *et al.*, 1983), Os₃(μ -H)[μ -SC(CH₃)₃](CO)₁₀ (Δ = 0.004 Å; Monari *et al.*, 1996), and Os₃(μ -H)-[μ -SC(HPh₂)](CO)₁₀ (Δ = 0.008 Å; Holden *et al.*, 1983).

Experimental

 $Os_3(\mu-H)(\mu-SPh)(CO)_{10}$ (90 mg, 0.094 mmol) or $Os_3(\mu-H)[\mu-S-(2-naphthyl)](CO)_{10}$ (95 mg, 0.094 mmol) were dissolved in a mixture of dichloromethane (15 ml) and acetonitrile (1 ml) under an argon atmosphere. Trimethylamine *N*-oxide (9 mg) was then added. After 1 h, the solvent was removed under reduced pressure and the crude

Compound (I)

Crystal data

$$\begin{split} & [\text{Os}_3\text{H}(\text{C}_6\text{H}_5\text{S})(\text{C}_{12}\text{H}_{23}\text{P})(\text{CO})_9] \\ & M_r = 1131.13 \\ & \text{Monoclinic, } C2/c \\ & a = 20.893 \text{ (3) Å} \\ & b = 9.010 \text{ (2) Å} \\ & c = 33.399 \text{ (5) Å} \\ & \beta = 91.04 \text{ (1)}^{\circ} \\ & V = 6286.2 \text{ (19) Å}^3 \\ & Z = 8 \end{split}$$

Data collection

Siemens P4 diffractometer ω scans Absorption correction: ψ scan (North *et al.*, 1968) $T_{min} = 0.146, T_{max} = 0.375$ 8816 measured reflections 7221 independent reflections 4147 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.045$ $wR(F^2) = 0.077$ S = 0.9247221 reflections 376 parameters H atoms treated by a mixture of independent and constrained

independent and constrained refinement

Table 1

Selected geometric parameters (Å, °) for (I).

Os1-P1	2.342 (3)	Os3-S1	2.412 (3)
Os1-Os2	2.8382 (7)	S1-C31	1.803 (10)
Os1-Os3	2.8678 (7)	Os2-H2	1.86 (8)
Os2-S1	2.413 (3)	Os3-H2	1.85 (8)
Os2–Os3	2.8674 (7)	P1-H1	1.54 (10)
P1-Os1-Os2	160.59 (7)	Os1-Os2-Os3	60.344 (18)
P1-Os1-Os3	100.43 (7)	S1-Os3-Os2	53.56(7)
Os2-Os1-Os3	60.332 (18)	S1-Os3-Os1	83.72 (7)
S1-Os2-Os1	84.34 (7)	Os2-Os3-Os1	59.324 (17)
S1 - Os2 - Os3	53.52 (7)	Os3-S1-Os2	72.92 (8)

Compound (II)

Crystal data	
$[Os_3H(C_{10}H_7S)(C_{12}H_{23}P)(CO)_9]$	Z = 2
$M_r = 1181.19$	$D_x = 2.265 \text{ Mg m}^{-3}$
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
a = 10.214 (2) Å	Cell parameters from 29
b = 12.997 (2) Å	reflections
c = 14.409(1) Å	$\theta = 14.60 - 34.89^{\circ}$
$\alpha = 69.16 \ (1)^{\circ}$	$\mu = 11.132 \text{ mm}^{-1}$
$\beta = 80.58 \ (1)^{\circ}$	T = 203 (2) K
$\gamma = 76.62 \ (1)^{\circ}$	Block, yellow
$V = 1732.2 (4) \text{ Å}^3$	$0.50 \times 0.15 \times 0.13 \text{ mm}$

metal-organic compounds

Data collection

Siemens P4 diffractometer ω scans Absorption correction: ψ scan (North *et al.*, 1968) $T_{min} = 0.126$, $T_{max} = 0.235$ 9107 measured reflections 7794 independent reflections 6138 reflections with $I > 2\sigma(I)$

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.040$ $wR(F^2) = 0.104$ S = 1.0297794 reflections 413 parameters H atoms treated by a mixture of independent and constrained refinement $\begin{aligned} R_{\text{int}} &= 0.019 \\ \theta_{\text{max}} &= 27.5^{\circ} \\ h &= -1 \rightarrow 13 \\ k &= -15 \rightarrow 15 \\ l &= -18 \rightarrow 18 \\ 3 \text{ standard reflections} \\ \text{every 397 reflections} \\ \text{intensity decay: 4\%} \end{aligned}$

$$\begin{split} &w = 1/[\sigma^2(F_o^2) + (0.0618P)^2] \\ &where \ P = (F_o^2 + 2F_c^2)/3 \\ &(\Delta/\sigma)_{\rm max} = 0.003 \\ &\Delta\rho_{\rm max} = 0.99 \ {\rm e}\ {\rm \AA}^{-3} \\ &\Delta\rho_{\rm min} = -0.91 \ {\rm e}\ {\rm \AA}^{-3} \\ & {\rm Extinction\ correction:\ SHELXTL/} \\ &NT\ ({\rm Siemens,\ 1995}) \\ &{\rm Extinction\ coefficient:\ 0.00020\ (14)} \end{split}$$

Table 2Selected geometric parameters (Å, °) for (II).

Os1-Os3	2.8544 (6)	Os3-S1	2.423 (2)
Os1-Os2	2.8928 (5)	S1-C31	1.798 (8)
Os2-P1	2.345 (2)	P1-H1	1.42 (10)
Os2-S1	2.434 (2)	Os2-H2	1.70 (11)
Os2-Os3	2.8585 (5)	Os3-H2	1.70 (12)
Os3-Os1-Os2	59.650 (14)	Os3-Os2-Os1	59.509 (14)
P1-Os2-S1	95.91 (7)	S1-Os3-Os1	82.68 (5)
P1-Os2-Os3	140.40 (6)	S1-Os3-Os2	54.12 (5)
S1-Os2-Os3	53.76 (5)	Os1-Os3-Os2	60.842 (14)
P1-Os2-Os1	94.91 (6)	Os3-S1-Os2	72.12 (6)
S1-Os2-Os1	81.68 (5)		
	()		

For both structures, the phosphine H atoms as well as the bridging H atoms were located from difference Fourier maps. Their positional parameters were refined and the isotropic displacement parameters were held fixed. Phenyl, cyclohexyl and naphpthyl H atoms were fixed at idealized positions. Refinement used a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$. The maximum residual electron-density peak in (I) was 1.2 Å from H36, while that in (II) was 1.0 Å from Os1.

For both compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL/NT* (Siemens, 1995); program(s) used to refine structure: *SHELXTL/NT*; molecular graphics: *SHELXTL/NT*; software used to prepare material for publication: *SHELXTL/NT*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1077). Services for accessing these data are described at the back of the journal.

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