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# Hydrido-sulfido-bridged triangular $\mathrm{Os}_{3}$ cluster compounds with different phosphine ligand substitution patterns 

Ulrich Flörke,* Hans Egold and Markus Schraa

Fachbereich Chemie und Chemietechnik, Universität-GH Paderborn, Warburgerstrasse 100, D-33098 Paderborn, Germany<br>Correspondence e-mail: uf@chemie.uni-paderborn.de

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In the course of our studies of trinuclear osmium cluster complexes with bridging sulfido and hydrido ligands, the new compounds $\mathrm{Os}_{3}(\mu-\mathrm{H})(\mu-\mathrm{SR})(\mathrm{CO})_{9}\left(\mathrm{PHCy}_{2}\right)(\mathrm{Cy}=$ cyclohexyl) with $R=$ phenyl, (I) (nonacarbonyl- $1 \kappa^{3} C, 2 \kappa^{3} C, 3 \kappa^{3} C$-dicyclo-hexylphosphine-3 $\kappa P$ - $\mu$-hydrido-1:2 $\kappa^{2} H$ - $\mu$-phenylthio-1:2 $2 \kappa^{2} S$ -triangulo-triosmium ), $\left[\mathrm{Os}_{3} \mathrm{H}\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~S}\right)\left(\mathrm{C}_{12} \mathrm{H}_{23} \mathrm{P}\right)(\mathrm{CO})_{9}\right]$, and $R=$ naphthyl, (II) [nonacarbonyl- $1 \kappa^{3} C, 2 \kappa^{2} C, 3 \kappa^{4} C$-dicyclohexyl-phosphine- $2 \kappa P-\mu$-hydrido-1:2 $\kappa^{2} H-\mu$-(2-naphthylthio) $-1: 2 \kappa^{2} S$ -triangulo-triosmium], $\left[\mathrm{Os}_{3} \mathrm{H}\left(\mathrm{C}_{10} \mathrm{H}_{7} \mathrm{~S}\right)\left(\mathrm{C}_{12} \mathrm{H}_{23} \mathrm{P}\right)(\mathrm{CO})_{9}\right]$, 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 $\mathrm{Os}_{3}(\mu-\mathrm{H})(\mu-\mathrm{S} R)(\mathrm{CO})_{10-n} L_{n}$ ( $n=0$ or 1 ) compounds show rather differing patterns of OsOs distances, and the positions of the $\mu-\mathrm{H}$ 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 $\mu-\mathrm{H}$ atoms.

(I)

(11)

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 $\mu-\mathrm{H}$ and $\mu-\mathrm{S}$ atoms as ligands. The CO groups show an
ecliptic arrangement, with torsion angles $\mathrm{C} 5-\mathrm{Os} 2-\mathrm{Os} 3-\mathrm{C} 7$ -0.2 (5), C6-Os2-Os3-C8-2.2 (7) and C4-Os2-Os3C9 -6.4 (6) ${ }^{\circ}$. The third metal atom, Os1, has two axially and one equatorially attached CO group, as well as an equatorially positioned $\mathrm{PHCy}_{2}$ 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 $\mathrm{Os}_{2} \mu$-H and $\mathrm{Os}_{2} \mu$-S planes form a dihedral angle of $52.0(1)^{\circ}$, and the dihedral angles with the central $\mathrm{Os}_{3}$ ring are 73.7 (1) ${ }^{\circ}$ for the $\mathrm{Os}_{2} \mu$-S plane and $125.7(1)^{\circ}$ for $\mathrm{Os}_{2} \mu-\mathrm{H}$. Two edges, Os1-Os3 of 2.8678 (7) and Os2-Os3 of 2.8674 (7) A. are equal and clearly longer than the Os1-Os2 edge of 2.8382 (7) A. One of the long edges is bridged by the two $\mu-\mathrm{H}$ and $\mu$-S ligands, and the short Os-Os edge has the $\mathrm{PHCy}_{2}$ 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 $\mathrm{Os}-\mathrm{S}$ bond lengths of 2.412 (3) and 2.413 (3) $\AA$, and compares well with that known from the above-mentioned related $\mathrm{Os}_{3}$ clusters. The $\mathrm{S}-\mathrm{C}_{\text {phenyl }}$ distance of 1.803 (10) $\AA$ is consistent with a single bond and the plane of the phenyl ring is nearly perpendicular to the $\mathrm{Os}_{3}$ plane at an angle of $85.0(1)^{\circ}$.

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 $\mu$-S ligand. The deciding difference, however, is the position of the $\mathrm{PHCy}_{2}$ group, which is pseudo-trans to the bridged Os-Os bond and is attached to Os 2 . The $\mathrm{Os} 2-\mathrm{P}$ bond length of 2.345 (2) $\AA$ is equal to that for (I) [2.342 (3) $\AA$ ] 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 $\mathrm{Os}_{2} \mu-\mathrm{H}$ and $\mathrm{Os}_{2} \mu$-S planes is $47.3(1)^{\circ}$ and the dihedral angles between the $\mathrm{Os}_{3}$ ring and $\mathrm{Os}_{2} \mu-\mathrm{S}$ and $\mathrm{Os}_{2} \mu-\mathrm{H}$ planes are 77.1 (1) and $124.4(1)^{\circ}$, respectively. The $\mathrm{Os}-\mathrm{S}$ bond lengths of 2.423 (2) and 2.434 (2) A differ only slightly and $\mathrm{S}-\mathrm{C}_{\text {naphthyl }}$ is 1.798 (8) $\AA$. However, the $\mathrm{Os}_{3}$ 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) $\AA$ and Os2-Os3 2.8585 (5) $\AA$, and one long Os1Os2 edge of 2.8928 (5) $\AA$. This latter edge is now cis to the $\mathrm{PHCy}_{2}$ ligand at Os2.


Figure 2
The molecular structure of (II) showing $50 \%$ probability displacement ellipsoids. Naphthyl and cyclohexyl H atoms have been omitted for clarity.

The $\mu-\mathrm{H}$ atoms of (I) and (II) have been located from difference Fourier maps and refined. Both lie above the $\mathrm{Os}_{3}$ planes if the $\mu$-S atoms are considered to lie below these planes. The mean Os -H bond lengths are 1.86 (8) $\AA$ for (I) and 1.70 (12) $\AA$ for (II).

The coordination geometry of (II) is just the same as for $\mathrm{Os}_{3}(\mu-\mathrm{H})(\mu-\mathrm{SPh})(\mathrm{CO})_{9}\left(\mathrm{PEt}_{3}\right)$, (III) (Ditzel et al., 1987), but in this complex, there are two long [2.883 (1) and 2.901 (1) $\AA$ ] and one short [2.862 (1) $\AA$ ] 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) $\AA$ ] is valid for the compound $\mathrm{Os}_{3}(\mu-\mathrm{H})\left(\mu-\mathrm{SCH}_{2} \mathrm{CH}=\mathrm{CH}_{2}\right)(\mathrm{CO})_{9}\left(\mathrm{PPh}_{3}\right)$, (IV) (Adams \& Pompeo, 1992), but here the phosphine ligand is cis to the $\mu-\mathrm{H}-\mu$-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 $0.015 \AA$ for (IV) to $0.032 \AA$ for (II), taking the reported s.u.'s into account. There is, however, no clear conjunction between the substitution pattern and the sequence of $\mathrm{Os}-\mathrm{Os}$ bonds. Related unsubstituted $\mathrm{Os}_{3}$ carbonyl compounds exhibit almost equal bond lengths for all three $\mathrm{Os}-\mathrm{Os}$ edges, e.g. $\mathrm{Os}_{3}(\mu-\mathrm{H})\left[\mu-\mathrm{SC}(\mathrm{H}) \mathrm{N}-p-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{~F}\right]-$ $(\mathrm{CO})_{10}$ (Adams \& Dawoodi, 1981) with a bond difference, $\Delta$, of $0.003 \AA, \quad \mathrm{Os}_{3}(\mu-\mathrm{H})\left(\mu-\mathrm{SC}=\mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{~S}\right)(\mathrm{CO})_{10} \quad(\Delta=$ 0.002 Å; Brodie et al., 1983), $\mathrm{Os}_{3}(\mu-\mathrm{H})\left[\mu-\mathrm{SC}\left(\mathrm{CH}_{3}\right)_{3}\right](\mathrm{CO})_{10}$ $\left(\Delta=0.004 \AA\right.$; Monari et al., 1996), and $\mathrm{Os}_{3}(\mu-\mathrm{H})$ -$\left[\mu-\mathrm{SC}\left(\mathrm{HPh}_{2}\right)\right](\mathrm{CO})_{10}(\Delta=0.008 \AA$ A ; Holden et al., 1983).

## Experimental

$\mathrm{Os}_{3}(\mu-\mathrm{H})(\mu-\mathrm{SPh})(\mathrm{CO})_{10}(90 \mathrm{mg}, \quad 0.094 \mathrm{mmol})$ or $\mathrm{Os}_{3}(\mu-\mathrm{H})[\mu-\mathrm{S}-$ (2-naphthyl)](CO) ${ }_{10}(95 \mathrm{mg}, 0.094 \mathrm{mmol})$ 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
material was purified by thin-layer chromatography (eluent: di-chloromethane- $n$-hexane, 1:10). The resulting product fractions contained a mixture of four isomers of $\mathrm{Os}_{3}(\mu-\mathrm{H})(\mu-\mathrm{SR})(\mathrm{CO})_{9}-$ $\left(\mathrm{PHCy}_{2}\right)$ ( $R=\mathrm{Ph}$ or naphthyl). Upon crystallization from $n$-pentane in both cases, single crystals of (I) and (II) were obtained.

## Compound (I)

Crystal data
$\left[\mathrm{Os}_{3} \mathrm{H}\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{~S}\right)\left(\mathrm{C}_{12} \mathrm{H}_{23} \mathrm{P}\right)(\mathrm{CO})_{9}\right.$ ]
$M_{r}=1131.13$
Monoclinic, $C 2 / c$
$a=20.893$ (3) A
$b=9.010(2) \AA$
$c=33.399$ (5) $\AA$
$\beta=91.04$ (1) ${ }^{\circ}$
$V=6286.2(19) \AA^{3}$
$Z=8$
$D_{x}=2.390 \mathrm{Mg} \mathrm{m}^{-3}$
Mo $K \alpha$ radiation
Cell parameters from 23

## reflections

$\theta=14.45-37.96^{\circ}$
$\mu=12.263 \mathrm{~mm}^{-1}$
$T=203$ (2) K
Block, yellow
$0.27 \times 0.14 \times 0.08 \mathrm{~mm}$
Data collection
Siemens $P 4$ diffractometer $\omega$ scans
Absorption correction: $\psi$ scan
$T_{\text {min }}=0.146, T_{\text {max }}=0.375$

$$
R_{\mathrm{int}}=0.047
$$

$$
\theta_{\max }=27.5^{\circ}
$$

$$
h=-27 \rightarrow 1
$$

(North et al., 1968)

$$
k=-1 \rightarrow 11
$$

8816 measured reflections
7221 independent reflections
4147 reflections with $I>2 \sigma(I)$
$l=-43 \rightarrow 43$
3 standard reflections every 397 reflections

## Refinement

Refinement on $F^{2}$
$w=1 /\left[\sigma^{2}\left(F_{o}{ }^{2}\right)+(0.0145 P)^{2}\right]$
where $P=\left(F_{o}{ }^{2}+2 F_{c}{ }^{2}\right) / 3$
$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.045$
$(\Delta / \sigma)_{\max }=0.001$
$w R\left(F^{2}\right)=0.077$
$S=0.924$
7221 reflections
376 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta \rho_{\text {max }}=0.91 \mathrm{e}^{\AA^{-3}}$
$\Delta \rho_{\min }=-0.98 \mathrm{e}^{-3}$

Table 1
Selected geometric parameters $\left(\AA^{\circ},{ }^{\circ}\right)$ 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

| $\left[\mathrm{Os}_{3} \mathrm{H}\left(\mathrm{C}_{10} \mathrm{H}_{7} \mathrm{~S}\right)\left(\mathrm{C}_{12} \mathrm{H}_{23} \mathrm{P}\right)(\mathrm{CO})_{9}\right]$ | $Z=2$ |
| :--- | :--- |
| $M_{r}=1181.19$ | $D_{x}=2.265 \mathrm{Mg} \mathrm{m}^{-3}$ |
| Triclinic, $P \overline{1}$ | Mo $K \alpha$ radiation |
| $a=10.214(2) \AA$ | Cell parameters from 29 |
| $b=12.997(2) \AA$ | reflections |
| $c=14.409(1) \AA$ | $\theta=14.60-34.89^{\circ}$ |
| $\alpha=69.16(1)^{\circ}$ | $\mu=11.132 \mathrm{~mm}^{-1}$ |
| $\beta=80.58(1)^{\circ}$ | $T=203(2) \mathrm{K}$ |
| $\gamma=76.62(1)^{\circ}$ | Block, yellow |
| $V=1732.2(4) \AA^{\circ}$ | $0.50 \times 0.15 \times 0.13 \mathrm{~mm}$ |

## Data collection

## Siemens $P 4$ diffractometer

$\omega$ scans
Absorption correction: $\psi$ scan
(North et al., 1968)
$T_{\text {min }}=0.126, T_{\text {max }}=0.235$
9107 measured reflections
7794 independent reflections
6138 reflections with $I>2 \sigma(I)$

## Refinement

Refinement on $F^{2}$
$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.040$
$w R\left(F^{2}\right)=0.104$
$S=1.029$
7794 reflections
413 parameters
H atoms treated by a mixture of independent and constrained refinement
$R_{\text {int }}=0.019$
$\theta_{\text {max }}=27.5^{\circ}$
$h=-1 \rightarrow 13$
$k=-15 \rightarrow 15$
$l=-18 \rightarrow 18$
3 standard reflections every 397 reflections intensity decay: 4\%
$w=1 /\left[\sigma^{2}\left(F_{o}{ }^{2}\right)+(0.0618 P)^{2}\right]$
where $P=\left(F_{o}{ }^{2}+2 F_{c}{ }^{2}\right) / 3$
$(\Delta / \sigma)_{\max }=0.003$
$\Delta \rho_{\max }=0.99 \mathrm{e}^{\AA^{-3}}$
$\Delta \rho_{\text {min }}=-0.91 \mathrm{e}^{-3}$
Extinction correction: SHELXTL/
$N T$ (Siemens, 1995)
Extinction coefficient: 0.00020 (14)

Table 2
Selected geometric parameters $\left(\AA^{\circ},{ }^{\circ}\right)$ 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 $U_{\text {iso }}(\mathrm{H})=1.2 U_{\text {eq }}(\mathrm{C})$. The maximum residual electron-density peak in (I) was $1.2 \AA$ from H36, while that in (II) was $1.0 \AA$ from Os1.

For both compounds, data collection: XSCANS (Siemens, 1994); cell refinement: $X S C A N S$; data reduction: $X S C A N S$; program(s) used to solve structure: $S H E L X T L / N T$ (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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