



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 Os₃(μ -H)(μ -SPh)(CO)₉(PET₃), (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 Os₃(μ -H)(μ -SCH₂CH=CH₂)(CO)₉(PPh₃), (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

Os₃(μ -H)(μ -SPh)(CO)₁₀ (90 mg, 0.094 mmol) or Os₃(μ -H)[μ -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

material was purified by thin-layer chromatography (eluent: dichloromethane-*n*-hexane, 1:10). The resulting product fractions contained a mixture of four isomers of Os₃(μ -H)(μ -SR)(CO)₉-(PhCy₂) (*R* = Ph or naphthyl). Upon crystallization from *n*-pentane in both cases, single crystals of (I) and (II) were obtained.

Compound (I)

Crystal data

[Os₃H(C₆H₅S)(C₁₂H₂₃P)(CO)₉]
M_r = 1131.13
 Monoclinic, *C2/c*
a = 20.893 (3) Å
b = 9.010 (2) Å
c = 33.399 (5) Å
 β = 91.04 (1)°
V = 6286.2 (19) Å³
Z = 8

D_x = 2.390 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 23 reflections
 θ = 14.45–37.96°
 μ = 12.263 mm⁻¹
T = 203 (2) K
 Block, yellow
 0.27 × 0.14 × 0.08 mm

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 σ (*I*)

R_{int} = 0.047
 θ_{max} = 27.5°
h = -27 → 1
k = -1 → 11
l = -43 → 43
 3 standard reflections
 every 397 reflections
 intensity decay: 5%

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.045
wR(*F*²) = 0.077
S = 0.924
 7221 reflections
 376 parameters
 H atoms treated by a mixture of independent and constrained refinement

w = 1/[$\sigma^2(F_o^2) + (0.0145P)^2$]
 where *P* = (*F_o*² + 2*F_c*²)/3
 $(\Delta/\sigma)_{\text{max}}$ = 0.001
 $\Delta\rho_{\text{max}}$ = 0.91 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.98 e Å⁻³

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

[Os₃H(C₁₀H₇S)(C₁₂H₂₃P)(CO)₉]
M_r = 1181.19
 Triclinic, *P1*
a = 10.214 (2) Å
b = 12.997 (2) Å
c = 14.409 (1) Å
 α = 69.16 (1)°
 β = 80.58 (1)°
 γ = 76.62 (1)°
V = 1732.2 (4) Å³

Z = 2
D_x = 2.265 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 29 reflections
 θ = 14.60–34.89°
 μ = 11.132 mm⁻¹
T = 203 (2) K
 Block, yellow
 0.50 × 0.15 × 0.13 mm

Data collection

Siemens P4 diffractometer	$R_{\text{int}} = 0.019$
ω scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -1 \rightarrow 13$
$T_{\text{min}} = 0.126$, $T_{\text{max}} = 0.235$	$k = -15 \rightarrow 15$
9107 measured reflections	$l = -18 \rightarrow 18$
7794 independent reflections	3 standard reflections
6138 reflections with $I > 2\sigma(I)$	every 397 reflections intensity decay: 4%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0618P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.040$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.104$	$(\Delta/\sigma)_{\text{max}} = 0.003$
$S = 1.029$	$\Delta\rho_{\text{max}} = 0.99 \text{ e } \text{\AA}^{-3}$
7794 reflections	$\Delta\rho_{\text{min}} = -0.91 \text{ e } \text{\AA}^{-3}$
413 parameters	Extinction correction: <i>SHELXTL/</i>
H atoms treated by a mixture of independent and constrained refinement	<i>NT</i> (Siemens, 1995)
	Extinction coefficient: 0.00020 (14)

Table 2

Selected geometric parameters (\AA , $^\circ$) 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 naphthyl H atoms were fixed at idealized positions. Refinement used a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The maximum residual electron-density peak in (I) was 1.2 \AA^{-3} from H36, while that in (II) was 1.0 \AA^{-3} 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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