Acta Cryst. (1983). C**39**, 1197–1200

Reactions of $H_2Os_3(CO)_9NMe_3$ with Thiobenzophenone: Structures of 1,1,2,2,3,3,3,3-Octacarbonyl-1,2;2,3-di-μ-hydrido-1,2-μ-(mercapto)diphenylethanalato(2—)-μ-*S*:*C*′-1-thiobenzophenone-*triangulo*-triosmium, $C_{35}H_{22}O_9Os_3S_2$, and 1,1,2,2,2,3,3,3,3-Nonacarbonyl-1,2-μ-diphenylmethylthiolato-1,2-μ-hydrido-1-thiobenzophenone-*triangulo*-triosmium, $C_{35}H_{22}O_9Os_3S_2$

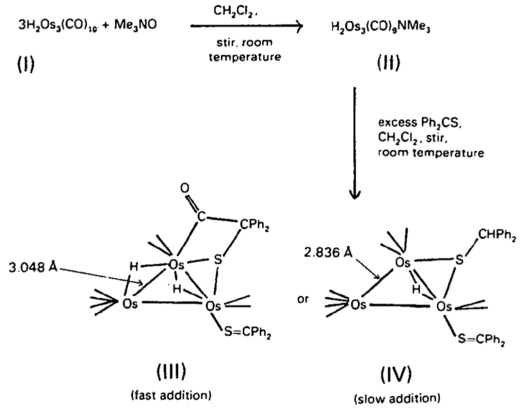
By H. Diane Holden, Brian F. G. Johnson, Jack Lewis,* Paul R. Raithby and George Uden

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

(*Received* 17 *November* 1982; *accepted* 30 *March* 1983)

Abstract. (III), $M_r = 1221{\cdot}3$, monoclinic, $I2/c$, $a = 31{\cdot}967\,(14)$, $b = 12{\cdot}509\,(7)$, $c = 19{\cdot}839\,(10)$ Å, $\beta = 101{\cdot}52\,(4)°$, $U = 7773{\cdot}6\,(69)$ Å^3, $Z = 8$, $D_x = 2{\cdot}09$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 9{\cdot}92$ mm^{-1}, $F(000) = 4511$, $T = 298$ K. The structure refined to $R = 0{\cdot}0486$ for 3889 unique diffractometer data. (IV), $M_r = 1221{\cdot}3$, monoclinic, $P2_1/n$, $a = 11{\cdot}811\,(3)$, $b = 13{\cdot}100\,(14)$, $c = 23{\cdot}573\,(8)$ Å, $\beta = 99{\cdot}40\,(2)°$, $U = 3598{\cdot}2\,(41)$ Å^3, $Z = 4$, $D_x = 2{\cdot}25$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 10{\cdot}7$ mm^{-1}, $F(000) = 2255$, $T = 298$ K. The structure refined to $R = 0{\cdot}0548$ for 4935 unique diffractometer data. (III) consists of a *triangulo*-triosmium unit with —S=CPh$_2$ attached to one metal. μ_2-bridging along one Os—Os edge is $>$S—$\overset{|}{\mathrm{C}}$Ph$_2$ with a ketonic carbonyl formed by attack of a neighbouring terminal —C≡O at this C atom. (IV) has a similar structure to (III) except all carbonyls present are terminal, and a hydride has migrated from an edge-bridging position in the Os$_3$ moiety to give (μ_2-SCHPh$_2$).

Introduction. As part of an investigation of the reactions of some triosmium clusters with thioorganic compounds, the molecular structures of the two title compounds have been determined. $H_2Os_3(CO)_{10}$ (I) reacts with Me$_3$NO in methylene dichloride at room temperature to give $H_2Os_3(CO)_9NMe_3$ (II) (Banford, 1982). (II) then reacts with excess thiobenzophenone: fast addition of the Ph$_2$CS gives (III) whilst slow addition at room temperature yields predominantly (IV) (Uden, 1982).



Experimental. Dark-red crystals of (III) obtained by slow recrystallization from hexane/CH$_2$Cl$_2$ were directly amenable to X-ray work; crystal size 1·1 × 1·9 × 1·5 mm. Syntex $P2_1$ automatic four-circle diffractometer, Mo $K\alpha$ radiation. Unit-cell dimensions found by least-squares fit to 15 intense reflections lying within shell $15 \le 2\theta \le 25°$. Intensity data measured for quadrant $+h$, $+k$, $\pm l$ ($3 \le 2\theta \le 50°$), $\omega/2\theta$ scans, variable scan speed. Backgrounds measured at each end of peak scan, two standard reflections after every 50 reflections. Lp corrections and semi-empirical absorption corrections, based on a pseudo-ellipsoid model, then applied. 3889 reflections [$F_o \ge 6\sigma(F_o)$] used in analysis. Structure solved by direct methods in $I2/c$ [non-standard setting of $C2/c$, systematic absences: hkl for $h + k + l$ odd, $h0l$ for $l(h)$ odd] using *SHELX*76 (Sheldrick, 1976); E map found positions for the three Os atoms, and thereafter difference syntheses found positions for all non-H atoms. During final cycles of blocked least-squares refinement on F^2, H atoms placed in calculated positions and, with Os and S atoms allowed anisotropic and the other atoms isotropic thermal parameters, R and R_g (unit weights) converged to 0·0486 and 0·0580. Complex neutral-atom scattering factors used for all atoms (*International Tables for X-ray Crystallography*, 1974).

Crystals of (IV) grown as dark shiny rhomboids from pentane. Data collection (crystal size 0·8 × 1·9 × 2·3 mm) for quadrant $+h$, $+k$, $\pm l$ and structure solution carried out in a manner directly analogous to that described above. Structure solved in $P2_1/n$ (non-standard setting of $P2_1/c$, systematic absences: $h0l$ for

---

* To whom correspondence should be addressed.

0108-2701/83/091197-04\$01.50

$h+l$ odd, $0k0$ for k odd) by direct methods for 4935 unique data having $F_o \geq 6\sigma(F_o)$; after suitable positions for the Os atoms found from E map, all other non-H atoms located. In final cycles of blocked-cascade least-squares refinement, with Os and S atoms anisotropic, R and R_g converged at 0·0548 and 0·0549.

Discussion. Fractional atomic coordinates, bond lengths and selected bond angles for compound (III) are given in Tables 1 and 2, for compound (IV) in Tables 3 and 4.* Figs. 1 and 2 show *PLUTO* (Motherwell, 1976) drawings of (III) and (IV) respectively.

The isomers (III) and (IV) reported here are both based on the familiar triangular Os_3 unit. The extended Os(1)—Os(3) distance of 3·048 (2) Å in (III), coupled with the carbonyl distribution, would indicate a (μ-H) lying along this edge, whilst the corresponding distance in (IV) is only 2·836 (2) Å.

In molecule (III) both hydrides lie along edges of the Os_3 unit, the second being along Os(1)—Os(2) [2·830 (2) Å], a situation also found in (IV) which has a bonding distance of 2·877 (2) Å.

Table 1. *Fractional coordinates* (× 10^4) *and isotropic temperature factors* (Å^2 × 10^3) *for compound* (III)

	x	y	z	U_{eq}/U_{iso}
Os(1)	1005 (1)	4243 (1)	10137 (1)	46 (1)*
Os(2)	1195 (1)	3066 (6)	9017 (1)	45 (1)*
Os(3)	506 (1)	2216 (1)	9652 (1)	51 (1)*
S(1)	1619 (2)	3117 (4)	10190 (3)	49 (3)*
S(2)	1484 (2)	1359 (4)	8929 (3)	58 (4)*
C(1)	1920 (6)	4424 (15)	10297 (9)	49 (5)
C(2)	1382 (7)	722 (17)	8181 (11)	52 (6)
C(111)	2124 (7)	4640 (16)	11042 (10)	51 (5)
C(112)	2274 (8)	5667 (21)	11213 (13)	78 (7)
C(113)	2429 (9)	5916 (25)	11903 (14)	93 (8)
C(114)	2469 (10)	5137 (25)	12392 (16)	99 (9)
C(115)	2336 (9)	4143 (26)	12235 (16)	102 (9)
C(116)	2163 (8)	3874 (23)	11540 (13)	84 (8)
C(121)	2270 (7)	4450 (16)	9869 (10)	52 (5)
C(122)	2502 (8)	3543 (20)	9803 (12)	70 (7)
C(123)	2850 (8)	3590 (22)	9480 (12)	78 (7)
C(124)	2962 (8)	4511 (20)	9216 (12)	77 (7)
C(125)	2745 (8)	5425 (20)	9269 (11)	69 (6)
C(126)	2394 (7)	5397 (18)	9596 (11)	64 (6)
C(211)	1247 (7)	1229 (16)	7517 (10)	54 (5)
C(212)	1468 (7)	2089 (18)	7328 (11)	63 (6)
C(213)	1357 (9)	2549 (22)	6682 (13)	85 (8)
C(214)	1015 (8)	2133 (21)	6230 (13)	82 (7)
C(215)	791 (9)	1298 (21)	6407 (13)	80 (7)
C(216)	901 (7)	837 (18)	7059 (11)	62 (6)
C(221)	1458 (7)	−450 (18)	8195 (11)	61 (6)
C(222)	1522 (8)	−948 (22)	7603 (14)	86 (8)
C(223)	1554 (10)	−2054 (27)	7576 (17)	108 (10)
C(224)	1554 (10)	−2580 (30)	8172 (18)	119 (11)
C(225)	1482 (11)	−2184 (30)	8754 (19)	128 (12)
C(226)	1415 (9)	−1047 (24)	8761 (15)	94 (9)
C(11)	618 (8)	5291 (20)	9932 (12)	70 (6)
O(11)	371 (6)	6023 (14)	9785 (8)	84 (5)
C(12)	1055 (8)	4531 (20)	11051 (13)	76 (7)
O(12)	1089 (6)	4677 (16)	11649 (10)	106 (6)
C(13)	1521 (7)	5177 (18)	10102 (11)	60 (6)
O(13)	1565 (5)	6119 (13)	9990 (8)	75 (4)
C(21)	1548 (7)	3850 (18)	8603 (11)	61 (6)
O(21)	1745 (5)	4388 (13)	8278 (8)	78 (5)
C(22)	798 (7)	3066 (17)	8199 (11)	60 (6)
O(22)	538 (5)	3090 (13)	7688 (8)	78 (5)
C(31)	445 (7)	1189 (18)	8953 (11)	64 (6)
O(31)	389 (6)	578 (16)	8487 (10)	105 (6)
C(32)	92 (9)	1759 (22)	10090 (14)	85 (8)
O(32)	−185 (6)	1369 (15)	10351 (9)	94 (6)
C(33)	144 (7)	3235 (19)	9101 (11)	65 (6)
O(33)	−80 (6)	3840 (14)	8767 (9)	87 (5)
C(34)	925 (9)	1388 (22)	10206 (14)	86 (8)
O(34)	1179 (6)	937 (16)	10617 (10)	101 (6)

*$U_{eq} = \frac{1}{3}$ of the trace of the orthogonalized **U** matrix.

Table 2. *Bond lengths* (Å) *and angles* (°) *for compound* (III)

Os(2)—Os(1)	2·830 (2)	Os(3)—Os(1)	3·048 (2)
Os(3)—Os(2)	2·947 (2)	S(1)—Os(1)	2·400 (5)
S(1)—Os(2)	2·450 (5)	S(2)—Os(2)	2·348 (5)
C(11)—Os(1)	1·794 (24)	C(12)—Os(1)	1·824 (26)
C(13)—Os(1)	2·033 (23)	C(21)—Os(2)	1·811 (24)
C(22)—Os(2)	1·949 (19)	C(31)—Os(3)	1·872 (23)
C(32)—Os(3)	1·813 (30)	C(33)—Os(3)	1·910 (22)
C(34)—Os(3)	1·869 (26)	C(1)—S(1)	1·888 (20)
C(2)—S(2)	1·659 (21)	C(111)—C(1)	1·515 (25)
C(121)—C(1)	1·534 (31)	C(13)—C(1)	1·572 (29)
C(211)—C(2)	1·448 (28)	C(221)—C(2)	1·485 (31)
C(112)—C(111)	1·389 (32)	C(116)—C(111)	1·365 (34)
C(113)—C(112)	1·395 (36)	C(114)—C(113)	1·363 (43)
C(115)—C(114)	1·330 (44)	C(116)—C(115)	1·420 (39)
C(122)—C(121)	1·377 (33)	C(126)—C(121)	1·394 (31)
C(123)—C(122)	1·389 (39)	C(124)—C(123)	1·344 (38)
C(125)—C(124)	1·354 (36)	C(126)—C(125)	1·403 (35)
C(212)—C(211)	1·379 (32)	C(216)—C(211)	1·373 (28)
C(213)—C(212)	1·386 (33)	C(214)—C(213)	1·369 (34)
C(215)—C(214)	1·354 (38)	C(216)—C(215)	1·395 (33)
C(222)—C(221)	1·380 (37)	C(226)—C(221)	1·379 (38)
C(223)—C(222)	1·389 (44)	C(224)—C(223)	1·354 (50)
C(225)—C(224)	1·317 (54)	C(226)—C(225)	1·439 (48)
O(11)—C(11)	1·205 (30)	O(12)—C(12)	1·184 (33)
O(13)—C(13)	1·212 (28)	O(21)—C(21)	1·194 (29)
O(22)—C(22)	1·176 (24)	O(31)—C(31)	1·186 (30)
O(32)—C(32)	1·213 (36)	O(33)—C(33)	1·156 (28)
O(34)—C(34)	1·173 (31)	S(2)···S(1)	3·295 (50)
Os(3)—Os(1)—Os(2)	60·1 (1)	S(1)—Os(1)—Os(2)	55·1 (1)
S(1)—Os(1)—Os(3)	84·1 (1)	C(11)—Os(1)—Os(2)	116·7 (7)
C(11)—Os(1)—Os(3)	104·0 (8)	C(11)—Os(1)—S(1)	163·8 (8)
C(12)—Os(1)—Os(2)	153·2 (8)	C(12)—Os(1)—Os(3)	114·5 (8)
C(12)—OS(1)—S(1)	99·4 (8)	C(12)—Os(1)—C(11)	90·0 (11)
C(13)—Os(1)—Os(2)	88·3 (6)	C(13)—Os(1)—Os(3)	147·7 (6)
C(13)—Os(1)—S(1)	71·2 (6)	C(13)—Os(1)—C(11)	95·7 (10)
C(13)—Os(1)—C(12)	90·5 (10)	Os(3)—Os(2)—Os(1)	63·6 (1)
S(1)—Os(2)—Os(1)	53·5 (1)	S(1)—Os(2)—Os(3)	85·5 (1)
S(2)—Os(2)—Os(1)	132·9 (1)	S(2)—Os(2)—Os(3)	92·4 (2)
S(2)—Os(2)—S(1)	86·7 (2)	C(21)—Os(2)—Os(1)	109·0 (7)
C(21)—Os(2)—Os(3)	167·5 (7)	C(21)—Os(2)—S(1)	98·0 (6)
C(21)—Os(2)—S(2)	99·7 (7)	C(22)—Os(2)—Os(1)	118·2 (7)
C(22)—Os(2)—Os(3)	86·3 (7)	C(22)—Os(2)—S(1)	170·5 (8)
C(22)—Os(2)—S(2)	98·4 (7)	C(22)—Os(2)—C(21)	89·0 (10)
Os(2)—Os(3)—Os(1)	56·3 (1)	C(31)—Os(3)—Os(1)	140·8 (7)
C(31)—Os(3)—Os(2)	84·6 (7)	C(32)—Os(3)—Os(1)	119·8 (8)
C(32)—Os(3)—Os(2)	176·1 (8)	C(32)—Os(3)—C(31)	99·3 (11)
C(33)—Os(3)—Os(1)	81·0 (7)	C(33)—Os(3)—Os(2)	86·1 (8)
C(33)—Os(3)—C(31)	94·2 (9)	C(33)—Os(3)—C(32)	94·0 (11)
C(34)—Os(3)—Os(1)	90·4 (8)	C(34)—Os(3)—Os(2)	86·6 (9)
C(34)—Os(3)—C(31)	90·6 (11)	C(34)—Os(3)—C(32)	92·9 (12)
C(34)—Os(3)—C(33)	170·9 (11)	Os(2)—S(1)—Os(1)	71·4 (1)
C(1)—S(1)—Os(1)	83·7 (6)	C(1)—S(1)—Os(2)	107·6 (6)
C(2)—S(2)—Os(2)	119·6 (8)	C(13)—C(1)—S(1)	96·9 (13)
C(111)—C(1)—S(1)	112·0 (13)	C(121)—C(1)—S(1)	111·6 (13)
C(13)—C(1)—C(111)	107·6 (16)	C(13)—C(1)—C(121)	119·8 (16)
C(121)—C(1)—C(111)	108·5 (16)	C(211)—C(2)—S(2)	125·0 (17)
C(221)—C(2)—S(2)	117·0 (15)	C(221)—C(2)—C(211)	117·9 (18)
O(11)—C(11)—Os(1)	177·0 (22)	O(12)—C(12)—Os(1)	177·5 (22)
C(1)—C(13)—Os(1)	105·7 (14)	O(13)—C(13)—Os(1)	133·7 (17)
O(13)—C(13)—C(1)	120·6 (19)	O(21)—C(21)—Os(2)	173·2 (18)
O(22)—C(22)—Os(2)	177·7 (20)	O(31)—C(31)—Os(3)	176·0 (19)
O(32)—C(32)—Os(3)	174·2 (23)	O(33)—C(33)—Os(3)	178·9 (21)
O(34)—C(34)—Os(3)	172·1 (25)		

---

* Lists of structure factors, anisotropic thermal parameters, phenyl-ring bond angles and H-atom coordinates for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38563 (58 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

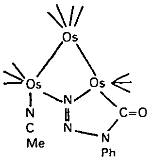
Further geometrical criteria for bridging hydrides along the Os(1)—Os(2) bonds are given by large Os—Os—C angles for *cis* carbonyl groups. In (III) angles Os(2)—Os(1)—C(12) and Os(1)—Os(2)—C(22) are 153·2 (8) and 118·2 (7)° respectively, whilst for compound (IV) the same angles are 118·2 (5) and 138·9 (5)° and Os(2)—Os(1)—C(13) is 134·2 (6)°. Thus, (IV) has one (μ-H), the second hydride being located as (μ-SCHPh$_2$) where the geometry at C(1) is tetrahedral.

(III) has tetrahedral geometry at C(1), reflecting the attack by a terminal —CO, giving a bridging carbonyl with the typically extended bond lengths of Os(1)—C(13) 2·033 (23), C(1)—C(13) 1·572 (29) and C(13)—O(13) 1·212 (28) Å. The geometry about C(13) is planar. Similar formation of a bridging carbonyl has been reported for (V) (Burgess, Johnson, Lewis & Raithby, 1982).

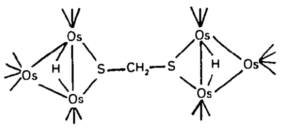
Table 3. *Fractional coordinates* (× 10^4) *and isotropic temperature factors* (Å^2 × 10^3) *for compound* (IV)

	x	*y*	*z*	U_{eq}/U_{iso}
Os(1)	6315 (1)	1024 (1)	2962 (1)	50 (1)*
Os(2)	6903 (1)	1730 (1)	4128 (1)	48 (1)*
Os(3)	6362 (1)	−351 (1)	3894 (1)	52 (1)*
S(1)	5108 (3)	1977 (3)	3497 (2)	52 (2)*
S(2)	7393 (4)	3469 (4)	4147 (2)	63 (3)*
C(1)	4822 (12)	3285 (11)	3196 (6)	49 (3)
C(111)	3989 (13)	3150 (12)	2643 (6)	55 (4)
C(112)	4155 (15)	3708 (13)	2158 (7)	69 (5)
C(113)	3383 (16)	3613 (14)	1639 (8)	78 (5)
C(114)	2501 (17)	2966 (16)	1618 (9)	87 (6)
C(115)	2292 (18)	2425 (16)	2082 (9)	90 (6)
C(116)	3017 (16)	2541 (14)	2591 (8)	76 (5)
C(121)	4411 (13)	3942 (12)	3634 (6)	58 (4)
C(122)	3658 (17)	3651 (16)	3971 (8)	85 (6)
C(123)	3295 (19)	4312 (17)	4385 (9)	96 (6)
C(124)	3724 (18)	5267 (17)	4445 (9)	94 (6)
C(125)	4478 (18)	5598 (17)	4094 (9)	95 (6)
C(126)	4808 (16)	4952 (14)	3674 (8)	77 (5)
C(2)	8614 (14)	3796 (12)	3992 (7)	60 (4)
C(211)	9408 (14)	3053 (13)	3791 (7)	65 (4)
C(212)	10262 (24)	2582 (22)	4178 (13)	131 (9)
C(213)	10969 (24)	1806 (22)	3923 (12)	130 (9)
C(214)	10785 (22)	1538 (20)	3400 (11)	115 (8)
C(215)	9997 (21)	2026 (19)	3023 (11)	109 (7)
C(216)	9318 (16)	2780 (14)	3225 (8)	74 (5)
C(221)	9006 (13)	4857 (12)	4060 (7)	59 (4)
C(222)	10123 (17)	5152 (16)	3983 (8)	84 (5)
C(223)	10489 (18)	6152 (16)	4042 (9)	89 (6)
C(224)	9787 (18)	6880 (18)	4183 (9)	94 (6)
C(225)	8684 (20)	6662 (19)	4282 (10)	107 (7)
C(226)	8299 (17)	5615 (15)	4208 (8)	82 (5)
C(11)	6457 (14)	2064 (13)	2429 (7)	61 (4)
O(11)	6644 (11)	2670 (10)	2088 (6)	89 (4)
C(12)	7364 (15)	241 (13)	2665 (7)	67 (4)
O(12)	8032 (12)	−223 (11)	2440 (6)	97 (4)
C(13)	5077 (15)	287 (14)	2556 (7)	69 (4)
O(13)	4231 (13)	−83 (12)	2322 (6)	104 (4)
C(21)	8238 (17)	1251 (16)	4563 (9)	84 (5)
O(21)	9038 (14)	990 (13)	4896 (7)	114 (5)
C(22)	6229 (15)	1843 (14)	4788 (8)	70 (4)
O(22)	5768 (12)	1888 (11)	5185 (6)	96 (4)
C(31)	7941 (14)	−448 (13)	3845 (7)	66 (4)
O(31)	8894 (11)	−533 (10)	3813 (5)	86 (4)
C(32)	6567 (19)	−821 (18)	4648 (10)	101 (7)
O(32)	6732 (18)	−1130 (16)	5124 (9)	155 (7)
C(33)	6020 (16)	−1587 (14)	3544 (8)	77 (5)
O(33)	5825 (13)	−2410 (12)	3332 (6)	107 (5)
C(34)	4781 (15)	−86 (13)	3872 (7)	64 (4)
O(34)	3789 (13)	58 (12)	3869 (6)	105 (4)

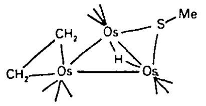
* U_{eq} (see Table 1).



(V)



(VI)



(VII)

Table 4. *Bond lengths* (Å) *and angles* (°) *for compound* (IV)

Os(1)—Os(2)	2·877 (2)	Os(1)—Os(3)	2·836 (2)
Os(1)—S(1)	2·403 (4)	Os(1)—C(11)	1·879 (16)
Os(1)—C(12)	1·833 (18)	Os(1)—C(13)	1·878 (17)
Os(2)—Os(3)	2·834 (2)	Os(2)—S(1)	2·406 (3)
Os(2)—S(2)	2·349 (5)	Os(2)—C(21)	1·844 (19)
Os(2)—C(22)	1·864 (19)	Os(3)—C(31)	1·892 (17)
Os(3)—C(32)	1·859 (24)	Os(3)—C(33)	1·832 (18)
Os(3)—C(34)	1·893 (17)	S(1)—C(1)	1·864 (15)
S(2)—C(2)	1·604 (17)	C(1)—C(111)	1·510 (19)
C(111)—C(112)	1·398 (23)	C(111)—C(116)	1·388 (24)
C(112)—C(111)	1·398 (23)	C(112)—C(113)	1·407 (23)
C(113)—C(114)	1·338 (28)	C(114)—C(115)	1·359 (30)
C(115)—C(116)	1·364 (26)	C(1)—C(121)	1·485 (22)
C(121)—C(122)	1·342 (27)	C(121)—C(126)	1·402 (24)
C(122)—C(123)	1·421 (31)	C(123)—C(124)	1·349 (31)
C(124)—C(125)	1·382 (32)	C(125)—C(126)	1·404 (30)
C(211)—C(212)	1·389 (31)	C(2)—C(211)	1·483 (24)
C(212)—C(213)	1·503 (42)	C(211)—C(216)	1·368 (25)
C(214)—C(215)	1·340 (34)	C(213)—C(214)	1·266 (38)
C(2)—C(221)	1·465 (22)	C(215)—C(216)	1·404 (32)
C(221)—C(226)	1·380 (26)	C(221)—C(222)	1·415 (26)
C(223)—C(224)	1·340 (32)	C(222)—C(223)	1·380 (29)
C(225)—C(226)	1·446 (31)	C(224)—C(225)	1·391 (33)
C(12)—O(12)	1·187 (24)	C(11)—O(11)	1·177 (22)
C(21)—O(21)	1·178 (24)	C(13)—O(13)	1·166 (22)
C(31)—O(31)	1·147 (22)	C(22)—O(22)	1·160 (24)
C(33)—O(33)	1·194 (24)	C(32)—O(32)	1·179 (32)
		C(34)—O(34)	1·186 (23)

Os(2)—Os(1)—Os(3)	59·5 (1)	Os(2)—Os(1)—S(1)	53·3 (1)
Os(3)—Os(1)—S(1)	82·0 (1)	Os(2)—Os(1)—C(11)	111·8 (5)
Os(3)—Os(1)—C(11)	170·5 (5)	S(1)—Os(1)—C(11)	95·7 (5)
Os(2)—Os(1)—C(12)	118·2 (5)	Os(3)—Os(1)—C(12)	90·6 (5)
S(1)—Os(1)—C(12)	170·9 (5)	C(11)—Os(1)—C(12)	90·7 (7)
Os(2)—Os(1)—C(13)	134·2 (6)	Os(3)—Os(1)—C(13)	89·0 (5)
S(1)—Os(1)—C(13)	93·1 (6)	C(11)—Os(1)—C(13)	100·4 (7)
C(12)—Os(1)—C(13)	92·2 (8)	Os(1)—Os(2)—Os(3)	59·5 (1)
Os(1)—Os(2)—S(1)	53·2 (1)	Os(3)—Os(2)—S(1)	82·0 (1)
Os(1)—Os(2)—S(2)	110·5 (1)	Os(3)—Os(2)—S(2)	169·6 (1)
S(1)—Os(2)—S(2)	94·1 (1)	Os(1)—Os(2)—C(21)	118·2 (7)
Os(3)—Os(2)—C(21)	85·8 (6)	S(1)—Os(2)—C(21)	167·6 (6)
S(2)—Os(2)—C(21)	97·7 (6)	Os(1)—Os(2)—C(22)	138·9 (5)
Os(3)—Os(2)—C(22)	97·2 (5)	S(1)—Os(2)—C(22)	93·0 (5)
S(2)—Os(2)—C(22)	92·6 (6)	C(21)—Os(2)—C(22)	90·4 (8)
Os(1)—Os(3)—Os(2)	61·0 (1)	Os(1)—Os(3)—C(31)	83·7 (5)
Os(2)—Os(3)—C(31)	83·3 (5)	Os(1)—Os(3)—C(32)	159·1 (7)
Os(2)—Os(3)—C(32)	98·2 (7)	C(31)—Os(3)—C(32)	93·5 (9)
Os(1)—Os(3)—C(33)	103·7 (6)	Os(2)—Os(3)—C(33)	164·6 (6)
C(31)—Os(3)—C(33)	93·5 (8)	C(32)—Os(3)—C(33)	97·1 (9)
Os(1)—Os(3)—C(34)	88·1 (5)	Os(2)—Os(3)—C(34)	91·1 (5)
C(31)—Os(3)—C(34)	171·6 (7)	C(32)—Os(3)—C(34)	93·5 (9)
C(33)—Os(3)—C(34)	90·3 (8)	Os(1)—S(1)—Os(2)	73·5 (1)
Os(1)—S(1)—C(1)	111·4 (5)	Os(2)—S(1)—C(1)	116·5 (4)
Os(2)—S(2)—C(2)	118·9 (6)	S(1)—C(1)—C(111)	105·8 (10)
S(1)—C(1)—C(121)	109·2 (10)	C(111)—C(1)—C(121)	115·3 (12)
S(2)—C(2)—C(211)	122·5 (12)	S(2)—C(2)—C(221)	120·6 (13)
C(211)—C(2)—C(221)	116·9 (14)	Os(1)—C(11)—O(11)	173·4 (14)
Os(1)—C(12)—O(12)	175·4 (15)	Os(1)—C(13)—O(13)	172·4 (17)
Os(2)—C(21)—O(21)	172·0 (19)	Os(2)—C(22)—O(22)	176·9 (13)
Os(3)—C(31)—O(31)	178·3 (15)	Os(3)—C(32)—O(32)	177·8 (21)
Os(3)—C(33)—O(33)	177·5 (17)	Os(3)—C(34)—O(34)	178·1 (14)

Both molecules have an $-S{=}CPh_2$ group attached to Os(2), are planar at C(2), and have short S(2)–C(2) distances of 1·659 (21) and 1·604 (17) Å for (III) and (IV). The Os(2)–S(2) distances [2·348 (5), 2·349 (5) Å] are slightly shorter than Os–S distances for the (μ-S) moieties, average values for which are 2·425 Å for (III) and 2·404 Å for (IV). Such Os–S distances are entirely in accord with those observed for (μ-S) in (VI) (Adams & Golembeski, 1979; Adams, Golembeski & Selegue, 1981) having an average value of 2·417 Å.

(VII) (Johnson, Lewis, Pippard & Raithby, 1980) also has a (μ-SCH_3) group with Os–S distances of 2·402 Å.

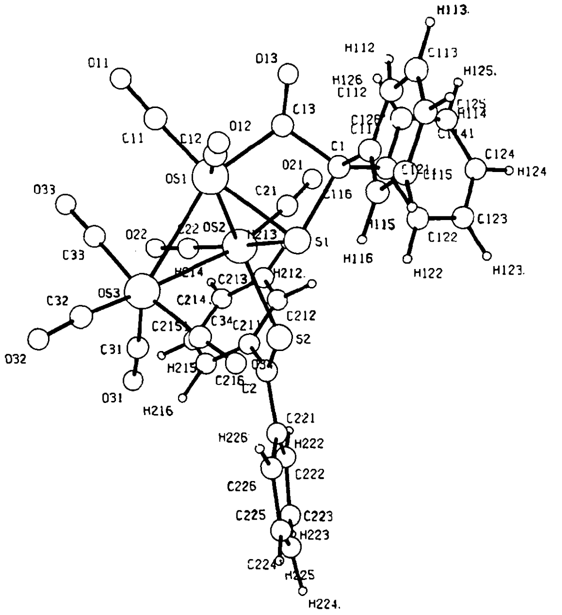


Fig. 1. Molecule (III) viewed perpendicular to the bridging carbonyl group.

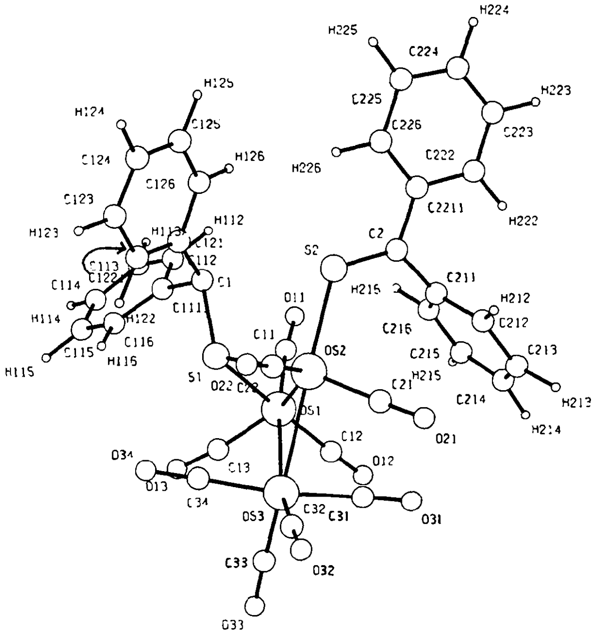


Fig. 2. A *PLUTO* drawing of molecule (IV).

References

ADAMS, R. D. & GOLEMBESKI, N. M. (1979). *J. Am. Chem. Soc.* **101**, 1306–1307.

ADAMS, R. D., GOLEMBESKI, N. M. & SELEGUE, J. P. (1981). *J. Am. Chem. Soc.* **103**, 546–555.

BANFORD, J. (1982). PhD Thesis, Univ. of Cambridge, England.

BURGESS, K., JOHNSON, B. F. G., LEWIS, J. & RAITHBY, P. R. (1982). *J. Organomet. Chem.* **224**, C40–C44.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, B. F. G., LEWIS, J., PIPPARD, D. C. & RAITHBY, P. R. (1980). *Acta Cryst.* B**36**, 703–705.

MOTHERWELL, W. D. S. (1976). *PLUTO*. Program for plotting molecular and crystalline structures. Univ. of Cambridge, England.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

UDEN, G. (1982). PhD Thesis, Univ. of Cambridge, England.

Acta Cryst. (1983). C**39**, 1200–1203

Structure of 1,1,1,2,2,2,3,3,3,3-Decacarbonyl-1,2-μ-diphenylmethylthiolato-1,2-μ-hydrido-*triangulo*-triosmium, $C_{23}H_{12}O_{10}Os_3S$

BY H. DIANE HOLDEN, BRIAN F. G. JOHNSON, JACK LEWIS,* PAUL R. RAITHBY AND GEORGE UDEN

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

(*Received* 17 *November* 1982; *accepted* 30 *March* 1983)

Abstract. $M_r = 1050{\cdot}95$, triclinic, space group $P\bar{1}$, $a = 9{\cdot}250\,(5)$, $b = 12{\cdot}274\,(8)$, $c = 13{\cdot}526\,(9)$ Å, $\alpha = 97{\cdot}55\,(5)$, $\beta = 94{\cdot}89\,(5)$, $\gamma = 117{\cdot}96\,(4)°$, $U = 1325{\cdot}7\,(14)$ Å^3, $Z = 2$, $D_x = 2{\cdot}63$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 14{\cdot}45$ mm^{-1}, $F(000) = 924$, $T = 298$ K. The structure refined to a final R of 0·0453

---

* To whom correspondence should be addressed.

0108-2701/83/091200-04$01.50