

Journal of Organometallic Chemistry, 140 (1977) 297-307
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THE MOLECULAR STRUCTURES OF $\text{H}_2\text{Os}_3(\text{CO})_{10}$, $\text{H}(\text{SC}_2\text{H}_5)\text{Os}_3(\text{CO})_{10}$ AND $(\text{OCH}_3)_2\text{Os}_3(\text{CO})_{10}$

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(Received May 11th, 1977)

Summary

X-ray crystallographic analyses of $\text{H}_2\text{Os}_3(\text{CO})_{10}$, $\text{H}(\text{SC}_2\text{H}_5)\text{Os}_3(\text{CO})_{10}$ and $(\text{OCH}_3)_2\text{Os}_3(\text{CO})_{10}$ are reported. Although hydrogen atom positions have not been located, the essential isostructural nature of the three complexes establishes the hydride ligands as bridging two metal atoms, separated by 2.670 Å, with a formal bond order of two; the bridging hydrido- and thiolato-ligands span an osmium-osmium bond of length 2.863 Å and formal bond order one; the two μ -methoxy ligands bridge two metal atoms separated by 3.078 Å which, by simple 18 electron rule counting, has a metal-metal bond order of zero. Some general comments are made on the structures of polynuclear transition metal carbonyls.

Introduction

There is much current interest in the chemistry of polynuclear carbonyls and, in particular, in the triangular clusters, $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Ru}, \text{Os}$). The latter show a variety of important oxidative addition and other reactions which may have some similarities to the events which accompany sorption of unsaturated ligands at transition metal surfaces [1,2]. Our interest in the bonding in clusters coincided with the synthesis, by Lewis and his colleagues, of a variety of complexes such as $\text{Os}_3(\text{CO})_{12}\text{Cl}_2$, $\text{Os}_3(\text{CO})_{10}\text{Cl}_2$ and, from the mild reaction of dihydrogen with $\text{Os}_3(\text{CO})_{12}$, the 'electron deficient' $\text{H}_2\text{Os}_3(\text{CO})_{10}$ [1]. The stereochemical consequences, on the metal-metal bonding, of changing the electronic properties of the ligands in the series $\text{L}_2\text{Os}_3(\text{CO})_{10}$ ($\text{L} = \text{H}, \text{OCH}_3, \text{SC}_2\text{H}_5$) is obviously of interest in quantifying aspects of the multicentre bonding in low-nuclearity cluster complexes; these are now reported in detail, an earlier summary having appeared some time ago [3].

Experimental

Crystal Data

(i) $\text{Os}_3(\text{CO})_{10}\text{H}_2$, Mol. wt. 852.7, Triclinic $a = 8.59(2)$, $b = 11.85(3)$, $c = 9.19(2)$ Å, $\alpha = 99.8(1)^\circ$, $\beta = 118.6(1)^\circ$, $\gamma = 81.0(1)^\circ$, $U = 806.9$ Å³ $Z = 2$, $D_c = 3.51$ g cm⁻³, $F(000) = 740$. Space group $P1$ (C_i^1 No. 1), or $P\bar{1}$ (C_i^1 No. 2). Mo- K_α radiation, $\mu = 250.2$ cm⁻¹.

(ii) $[\text{Os}_3(\text{CO})_{10}\text{HSC}_2\text{H}_5]$, $\text{Os}_3\text{C}_{12}\text{O}_{10}\text{SH}_6$, Mol. wt. 912.8, Orthorhombic, $a = 17.34(3)$, $b = 12.73(3)$, $c = 17.42(3)$ Å, $U = 3845$ Å³, $Z = 8$, $D_c = 3.15$ g cm⁻³, $F(000) = 3216$. Space group $Pbca$ (D_{2h}^8 , No. 61), Mo- K_α radiation, $\mu = 250.2$ cm⁻¹. The crystals are isomorphous with those of $\text{HSC}_2\text{H}_5\text{Ru}_3(\text{CO})_{10}$.

(iii) $[\text{Os}_3(\text{CO})_{10}(\text{OCH}_3)_2]$, $\text{Os}_3\text{C}_{12}\text{O}_{12}\text{H}_6$, Mol. wt. 912.8, Monoclinic $a = 12.44(3)$, $b = 9.01(2)$, $c = 17.19(3)$ Å, $\beta = 98.3(1)^\circ$, $U = 1921$ Å³, $Z = 4$, $D_c = 3.18$ g cm⁻³, $F(000) = 1608$. Space group $P2_1/c$ (C_2^5 h , No. 14), Mo- K_α radiation, $\mu = 211.7$ cm⁻¹.

Determination and refinement of the crystal structures

Integrated X-ray reflexion intensities for the dihydrido- and monohydrido-complexes were obtained on a PAILRED diffractometer (Mo- K_α ; graphite monochromator) operating in a 'w' scan regime. Scan ranges varied linearly from layer to layer; all reflexions where separate background intensities differed significantly ($\geq 3\sigma$) were discarded and only those with $F_0^2/\sigma(F_0^2) \geq 3.0$ were used for the structures' solutions and refinements. Absorption corrections were made, carrying out the integration by appropriate Gaussian quadrature. Intensities were estimated visually for the bis-methoxy complex, from Weissenberg and precession photographs (Mo- K_α); of the total data measured (2336), final refinement was based on the 1783 data estimated from precession photographs for which accurate absorption corrections could be applied.

Structures were solved via vector analysis of heavy atom positions and subsequent difference Fourier syntheses. Block diagonal least squares methods only were used (these analyses were completed in 1969!) and convergence was to $R_1 = 0.048$ (2440 independent reflexions) for $\text{H}_2\text{Os}_3(\text{CO})_{10}$, to $R_1 = 0.055$ (1270 independent reflexions) for $\text{HSC}_2\text{H}_5\text{Os}_3(\text{CO})_{10}$ and to $R_1 = 0.084$ (1783 independent reflexions) for $(\text{OCH}_3)_2\text{Os}_3(\text{CO})_{10}$. Atomic scattering factors used were those listed in the International Tables for X-ray Crystallography for the uncharged atoms. The Os scattering factors were corrected for the real component of anomalous dispersion. Tables of calculated and observed structure factors can be obtained from the authors (RM).

Discussion

Atomic positional and vibrational parameters are listed in Tables 1, 2, and 3, intramolecular bond lengths and bond angles are summarised in Tables 4 and 5. Atom labelling is depicted in Fig. 1, 2 and 3, which illustrate the general molecular stereochemistries.

There are two main features of the observed molecular geometries which deserve comment: the variation of essentially only one metal-metal interatomic distance with ligand changes and the implication that this feature has for discussions of bonding in cluster complexes in general and bridged metal-metal

(continued on p. 302)

TABLE I
 $\text{H}_2\text{O}_3(\text{CO})_0$: ATOMIC COORDINATES AND VIBRATION PARAMETERS (e.s.d.'s in parentheses)

Atom	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
O(1)	-0.20340(10)	0.28827(6)	0.18593(9)	0.01087(12)	0.00396(5)	0.00712(9)	-0.00078(10)	0.00878(17)	-0.00108(12)
O(2)	0.14885(10)	0.20276(6)	0.26458(9)	0.01081(13)	0.00465(5)	0.00766(9)	-0.00082(11)	0.00823(18)	-0.00076(13)
O(3)	-0.07279(11)	0.24898(6)	-0.04716(8)	0.01414(14)	0.00400(5)	0.00189(9)	-0.00058(10)	0.01087(18)	-0.00182(13)
C(1)	-0.4450(28)	0.3452(18)	0.0433(26)	0.0151(41)	0.0054(15)	0.0114(32)	-0.0024(35)	0.0018(57)	0.0023(39)
C(2)	-0.2255(30)	0.2967(19)	0.3854(26)	0.0170(44)	0.0066(17)	0.0120(32)	-0.0005(36)	0.0120(62)	-0.0058(42)
C(3)	-0.1114(30)	0.4343(16)	0.2456(27)	0.0189(44)	0.0047(14)	0.0171(37)	-0.0065(36)	0.0251(70)	-0.0044(38)
C(4)	-0.2514(31)	0.1284(20)	0.1185(28)	0.0164(44)	0.0084(19)	0.0152(37)	0.0017(42)	0.0209(57)	-0.0050(45)
C(5)	0.3692(30)	0.1431(21)	0.2688(26)	0.0137(41)	0.0095(21)	0.0106(32)	-0.0003(41)	0.0038(58)	-0.0071(46)
C(6)	0.1438(28)	0.0925(20)	0.3887(24)	0.0139(40)	0.0098(21)	0.0089(28)	0.0029(37)	0.0133(55)	-0.0022(44)
C(7)	0.2581(37)	0.3021(32)	0.4617(32)	0.0157(52)	0.0187(40)	0.0115(39)	-0.0039(62)	0.0013(70)	0.0097(71)
C(8)	0.0501(34)	0.2162(19)	-0.1694(26)	0.0234(53)	0.0070(17)	0.0113(32)	-0.0014(37)	0.0213(68)	-0.0058(47)
C(9)	-0.2754(38)	0.1803(20)	-0.2146(27)	0.0273(50)	0.0053(17)	0.0116(33)	-0.0022(38)	0.0176(73)	-0.0041(49)
C(10)	-0.1766(32)	0.3907(18)	-0.1280(26)	0.0228(50)	0.0076(17)	0.0135(34)	-0.0023(38)	0.0322(72)	-0.0066(46)
O(1)	-0.5803(23)	0.3785(18)	-0.0420(26)	0.0117(31)	0.0125(20)	0.0234(40)	-0.0001(45)	0.0095(56)	0.0071(39)
O(2)	-0.2467(30)	0.2986(19)	0.4974(20)	0.0326(54)	0.0159(24)	0.0095(25)	-0.0014(38)	0.0166(60)	-0.0143(55)
O(3)	-0.0419(26)	0.5200(13)	0.2851(24)	0.0255(42)	0.0054(12)	0.0250(39)	-0.0043(34)	0.0258(66)	-0.0085(35)
O(4)	-0.2734(29)	0.0314(14)	0.0642(25)	0.0317(50)	0.0059(13)	0.0251(40)	-0.0006(35)	0.0308(73)	-0.0106(39)
O(5)	0.5059(25)	0.1046(17)	0.2728(25)	0.0189(38)	0.0121(19)	0.0251(40)	-0.0023(43)	0.0298(65)	-0.0007(41)
O(6)	0.1438(31)	0.0269(20)	0.4610(25)	0.0315(54)	0.0144(23)	0.0214(39)	0.0139(48)	0.0327(76)	0.0040(54)
O(7)	0.3223(29)	0.3705(16)	0.5750(21)	0.0317(51)	0.0096(17)	0.0123(28)	-0.0140(51)	0.0015(59)	-0.0024(45)
O(8)	0.1435(27)	0.1968(16)	-0.2416(24)	0.0261(46)	0.0108(17)	0.0234(37)	-0.0020(35)	0.0385(70)	-0.0037(42)
O(9)	-0.3993(26)	0.1302(17)	-0.3101(21)	0.0214(40)	0.0126(20)	0.0123(27)	-0.0037(36)	0.0036(52)	-0.0091(43)
O(10)	-0.2647(32)	0.4746(14)	-0.1842(26)	0.0412(51)	0.0080(14)	0.0258(41)	0.0131(38)	0.0398(84)	0.0096(44)

The atom temperature factors take the form: $T = \exp(-b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}hl + b_{31}hl + b_{12}hk)$

TABLE 2
 $\text{H}(\text{SC}_2\text{H}_3\text{O}_3\text{CO})_2$: ATOM COORDINATES AND VIBRATIONAL PARAMETERS

Atom	x/a	y/b	z/c	$U(\text{\AA}^2)$	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
O ₁ (1)	0.17049(10)	0.30565(13)	0.19848(11)	5.80(18)	0.00227(1)	0.00465(2)	0.00285(1)	0.00218(0)	-0.00112(2)	-0.00076(2)
O ₂ (2)	0.09854(9)	0.21508(13)	0.06682(9)	6.32(20)	0.00227(1)	0.00408(1)	0.00233(1)	0.00054(0)	0.00050(2)	0.00079(2)
O ₃ (3)	0.09863(8)	0.27026(12)	0.19877(9)	3.43(13)	0.00213(1)	0.00367(1)	0.00187(1)	0.00039(0)	0.00019(1)	-0.00030(2)
S(1)	0.0162(6)	0.3052(8)	0.0791(6)	6.46(22)	0.00199(6)	0.00427(10)	0.00294(6)	0.00211(0)	-0.00026(10)	-0.00038(13)
C(1)	0.1850(29)	0.3554(41)	0.2989(34)	5.80(18)						
C(9)	0.2717(31)	0.2999(44)	0.1862(34)	6.32(20)						
C(3)	0.1520(24)	0.4443(32)	0.1666(25)	3.43(13)						
C(4)	0.1769(23)	0.1724(30)	0.2380(24)	3.12(12)						
C(5)	0.0388(32)	0.1578(45)	-0.0129(35)	6.46(22)						
C(6)	0.1663(30)	0.0871(41)	0.0814(32)	5.06(19)						
C(7)	0.1674(27)	0.2522(38)	0.0011(27)	4.63(15)						
C(8)	-0.0953(23)	0.2352(33)	0.1931(26)	4.22(14)						
C(9)	0.0210(22)	0.1881(32)	0.2880(25)	3.71(14)						
C(10)	-0.0099(24)	0.3924(32)	0.2579(26)	3.63(13)						
C(11)	-0.0774(24)	0.3453(34)	0.0260(26)	3.86(15)						
C(12)	-0.1392(25)	0.4285(35)	0.0563(28)	4.14(15)						
O(1)	0.1881(21)	0.3950(31)	0.3580(25)	7.10(16)						
O(2)	0.3337(23)	0.2985(32)	0.1387(25)	7.69(15)						
O(3)	0.1432(19)	0.5321(26)	0.1488(21)	5.52(13)						
O(4)	0.1892(18)	0.0815(20)	0.2527(21)	5.26(12)						
O(5)	0.0015(26)	0.1186(38)	-0.0604(30)	9.56(19)						
O(6)	0.1927(23)	0.0170(32)	0.0737(27)	7.68(16)						
O(7)	0.2196(19)	0.3232(27)	-0.0327(22)	6.04(13)						
O(8)	-0.1653(19)	0.1975(26)	0.1841(21)	5.92(12)						
O(9)	0.0333(17)	0.1387(24)	0.3462(19)	4.79(11)						
O(10)	-0.0295(22)	0.4666(26)	0.2984(25)	6.82(15)						

TABLE 3
 $(\text{OCl}_2)_2\text{O}_3(\text{CO})_{10}$: ATOM COORDINATES AND VIBRATIONAL PARAMETERS

Atom	x/a	y/b	z/c	$B(\text{\AA}^2)$	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
O ₁ (1)	0.19598(16)	0.24562(17)	0.21952(11)		0.00553(2)	0.01080(3)	0.00370(1)	-0.00006(0)	0.00524(5)	0.00086(4)
O ₁ (2)	0.26404(10)	0.33993(16)	0.09037(10)		0.00673(2)	0.00997(2)	0.00346(1)	0.00019(0)	0.00392(5)	-0.00212(4)
O ₁ (3)	0.20641(16)	0.01119(16)	0.13547(11)		0.00695(2)	0.00968(2)	0.00376(1)	-0.00018(0)	0.00490(5)	-0.00031(4)
C(1)	0.1996(40)	0.1268(47)	0.2988(27)	5.2(2)						
C(2)	0.1660(48)	0.4409(58)	0.2506(33)	7.2(2)						
C(3)	0.0550(40)	0.2328(46)	0.1474(26)	5.0(2)						
C(4)	0.3257(31)	0.2554(32)	0.2755(19)	2.7(1)						
C(5)	0.3495(37)	0.3987(44)	0.0017(25)	4.7(1)						
C(6)	0.8612(33)	0.4819(38)	0.1623(22)	3.7(1)						
C(7)	0.1688(44)	0.4829(53)	0.0690(30)	5.2(2)						
C(8)	0.3235(43)	-0.1296(52)	0.0708(29)	6.0(2)						
C(9)	0.3276(43)	-0.0735(52)	0.2278(29)	6.0(2)						
C(10)	0.1448(38)	-0.0839(46)	0.1505(25)	4.9(2)						
C(11)	0.2080(43)	0.1076(53)	-0.0381(30)	6.1(2)						
C(12)	0.4782(46)	0.1314(55)	0.0957(31)	6.6(2)						
O(1)	0.1097(31)	0.0451(38)	0.3405(21)	7.3(1)						
O(2)	0.1312(35)	0.5596(43)	0.2675(24)	8.8(2)						
O(3)	-0.0195(32)	0.2171(37)	0.0988(21)	7.1(1)						
O(4)	0.4134(28)	0.2889(32)	0.3080(18)	5.5(1)						
O(5)	0.3918(31)	0.4329(37)	-0.0530(21)	7.0(1)						
O(6)	0.3963(29)	0.5710(35)	0.1971(19)	6.4(1)						
O(7)	0.1019(29)	0.5591(34)	0.0476(20)	6.4(1)						
O(8)	0.3552(33)	-0.2317(40)	0.0392(22)	7.7(2)						
O(9)	0.3693(30)	-0.1227(36)	0.2882(20)	6.8(1)						
O(10)	0.0549(29)	-0.1523(35)	0.1449(20)	6.5(1)						
O(11)	0.1993(26)	0.1507(31)	0.0462(18)	5.4(1)						
O(12)	0.3907(22)	0.1662(26)	0.1280(15)	3.7(1)						

TABLE 4

Os₃(CO)₁₀L₂: INTRAMOLECULAR BOND LENGTHS (Å) AND THEIR STANDARD DEVIATIONS

Atoms	Os ₃ (CO) ₁₀ H ₂	Os ₃ (CO) ₁₀ SC ₂ H ₅ H	Os ₃ (CO) ₁₀ (OCH ₃) ₂
Os ₁ —Os ₂	2.813(1)	2.856(2)	2.815(3)
Os ₁ —Os ₃	2.804(1)	2.842(2)	2.823(3)
Os ₂ —Os ₃	2.670(1)	2.863(2)	3.078(3)
Os ₁ —C ₁	1.94(2)	1.88(5)	1.89(5)
Os ₁ —C ₂	1.92(2)	1.84(5)	1.89(6)
Os ₁ —C ₃	1.90(2)	1.88(4)	1.90(5)
Os ₁ —C ₄	1.93(3)	1.81(4)	1.86(3)
Os ₂ —C ₅	1.90(2)	1.88(6)	1.90(4)
Os ₂ —C ₆	1.89(2)	1.93(5)	1.84(4)
Os ₂ —C ₇	1.88(3)	1.86(5)	1.92(5)
Os ₃ —C ₈	1.91(3)	1.86(4)	1.89(5)
Os ₃ —C ₉	1.87(3)	1.89(4)	1.82(5)
Os ₃ —C ₁₀	1.87(2)	1.89(4)	1.79(4)
C ₁ —O ₁	1.10(3)	1.15(7)	1.13(6)
C ₂ —O ₂	1.12(3)	1.18(7)	1.16(7)
C ₃ —O ₃	1.17(3)	1.18(5)	1.16(6)
C ₄ —O ₄	1.16(3)	1.22(5)	1.16(5)
C ₅ —O ₅	1.18(3)	1.16(7)	1.18(6)
C ₆ —O ₆	1.12(3)	1.10(7)	1.15(5)
C ₇ —O ₇	1.16(4)	1.20(6)	1.10(6)
C ₈ —O ₈	1.16(3)	1.16(5)	1.17(6)
C ₉ —O ₉	1.14(3)	1.21(5)	1.18(6)
C ₁₀ —O ₁₀	1.16(3)	1.15(6)	1.27(6)
Os ₂ —O ₁₁			2.09(3)
Os ₂ —O ₁₂			2.09(3)
Os ₃ —O ₁₁			2.06(3)
Os ₃ —O ₁₂			2.10(3)
O ₁₁ —C ₁₁			1.52(6)
O ₁₂ —C ₁₂			1.33(6)
Os ₂ —S ₁		2.39(1)	
Os ₃ —S ₁		2.41(1)	
S ₁ —C ₁₁		1.89(4)	
C ₁₁ —C ₁₂		1.60(6)	

bonds in particular; and the general ligand arrangement around the metal polyhedron and its implications for models which place emphasis on non-valence interligand forces as a major structure-determining feature in low-nuclearity clusters [4].

Although the eighteen-electron rule [3,5] has less general validity in cluster complexes than obtains in mononuclear species, it is obvious that adherence of the present complexes to the rule would predict bond orders of two, one and zero for the Os(2)—Os(3) metal—metal bonds in H₂Os₃(CO)₁₀, HSEtOs₃(CO)₁₀ and (OMe)₂Os₃(CO)₁₀ respectively; the near-linear variation in the bond lengths is anticipated then from the general characteristics of the bond order—bond length relation [6]. But the Os(2)—Os(3) bond length variations in the series do not unequivocally establish the hydrido-ligands in H₂Os₃(CO)₁₀ as bridging, occupying structurally equivalent positions to the thiolato- and methoxy-bridges in HSC₂H₅Os₃(CO)₁₀ and (OCH₃)Os₃(CO)₁₀. That they are, in essence, symmetrical bridging hydrides is suggested strongly, however, by two other facts: if the hydride ligands in H₂Os₃(CO)₁₀ were terminal (to atoms Os(2) and Os(3)), one could imagine given the strong *trans*-influence of the hydride ligand, a significant

TABLE 5

Os₃(CO)₁₀L₂: INTRAMOLECULAR BOND ANGLES (degrees) AND THEIR STANDARD DEVIATIONS

Atoms	Os ₃ (CO) ₁₀ H ₂	Os ₃ (CO) ₁₀ SC ₂ H ₃ H	Os ₃ (CO) ₁₀ (OCH ₃) ₂
Os ₂ -Os ₁ -Os ₃	56.76(0.03)	60.33(0.06)	66.17(0.07)
Os ₁ -Os ₂ -Os ₃	61.46(0.03)	59.60(0.06)	57.04(0.06)
Os ₁ -Os ₃ -Os ₂	61.78 (0.03)	60.07(0.06)	56.79(0.06)
C ₁ -Os ₁ -Os ₃	99.0(0.07)	100.6(1.6)	96.5(1.4)
C ₂ -Os ₁ -Os ₂	106.8(0.7)	99.0(1.7)	93.9(1.7)
C ₁ -Os ₁ -C ₂	97.5(1.0)	99.8(2.3)	103.4(2.2)
C ₃ -Os ₁ -Os ₂	84.2(0.7)	93.9(1.2)	86.2(1.4)
C ₃ -Os ₁ -Os ₃	86.3(0.7)	88.9(1.2)	87.4(1.4)
C ₄ -Os ₁ -Os ₂	84.1(0.8)	86.0(1.2)	85.1(1.0)
C ₄ -Os ₁ -Os ₃	83.5(0.8)	84.9(1.2)	85.8(1.0)
C ₁ -Os ₁ -C ₃	94.7(1.0)	88.9(2.0)	96.5(1.0)
C ₁ -Os ₁ -C ₄	94.1(1.0)	88.9(2.0)	90.8(1.7)
C ₂ -Os ₁ -C ₃	93.2(1.0)	96.3(2.1)	93.2(2.2)
C ₂ -Os ₁ -C ₄	94.5(1.0)	90.7(2.1)	91.0(2.0)
C ₅ -Os ₂ -Os ₃	106.6(0.8)	112.8(1.7)	121.6(1.3)
C ₅ -Os ₂ -C ₆	96.1(1.0)	93.3(2.3)	91.3(1.8)
C ₅ -Os ₂ -C ₇	93.1(1.3)	94.5(2.2)	93.1(2.0)
C ₆ -Os ₂ -Os ₁	91.4(0.7)	90.4(1.6)	90.2(1.2)
C ₆ -Os ₂ -Os ₃	130.5(0.7)	112.6(1.6)	124.9(1.2)
C ₆ -Os ₂ -C ₇	90.2(1.2)	97.6(2.1)	87.6(1.9)
C ₇ -Os ₂ -Os ₁	96.3(1.0)	91.6(1.4)	87.5(1.5)
C ₇ -Os ₂ -Os ₃	130.5(1.0)	136.9(1.4)	127.9(1.5)
C ₈ -Os ₃ -Os ₂	107.1(0.8)	115.1(1.3)	116.8(1.5)
C ₈ -Os ₃ -C ₉	95.4(1.1)	91.2(1.8)	95.0(2.2)
C ₈ -Os ₃ -C ₁₀	94.5(1.1)	93.5(1.8)	99.3(2.1)
C ₉ -Os ₃ -Os ₁	93.6(0.8)	88.7(1.2)	90.1(1.6)
C ₉ -Os ₃ -Os ₂	131.7(0.8)	117.6(1.2)	125.9(1.6)
C ₉ -Os ₃ -C ₁₀	89.2(1.1)	91.5(1.7)	86.0(2.1)
C ₁₀ -Os ₃ -Os ₁	92.3(0.7)	92.2(1.2)	85.1(1.4)
C ₁₀ -Os ₃ -Os ₂	129.4(0.7)	137.0(1.2)	126.1(1.4)
Os ₁ -C ₁ -O ₁	177.3(2.2)	172.1(4.7)	173.1(4.1)
Os ₁ -C ₂ -O ₂	176.2(2.6)	173.5(4.8)	175.9(4.9)
Os ₁ -C ₃ -O ₃	174.8(2.1)	177.5(3.6)	173.6(4.1)
Os ₁ -C ₄ -O ₄	177.0(2.3)	171.3(3.4)	176.1(3.1)
Os ₂ -C ₅ -O ₅	178.8(2.2)	177.0(5.1)	178.6(3.8)
Os ₂ -C ₆ -O ₆	178.4(2.3)	165.0(4.8)	169.7(3.5)
Os ₂ -C ₇ -O ₇	174.3(2.8)	170.3(3.9)	171.5(4.6)
Os ₃ -C ₈ -O ₈	178.9(2.3)	168.2(3.7)	169.8(4.4)
Os ₃ -C ₉ -O ₉	176.5(2.4)	175.8(3.4)	177.2(4.4)
Os ₃ -C ₁₀ -O ₁₀	174.2(2.3)	172.0(3.8)	167.5(3.7)
O ₁₁ -Os ₂ -O ₁₂			76.5(1.1)
O ₁₁ -Os ₃ -O ₁₂			76.8(1.1)
Os ₂ -O ₁₁ -Os ₃			95.7(1.3)
Os ₂ -O ₁₂ -Os ₃			94.4(1.0)
Os ₂ -O ₁₁ -C ₁₁			117.0(2.6)
Os ₂ -O ₁₂ -C ₁₂			124.6(2.8)
Os ₃ -O ₁₁ -C ₁₁			118.5(2.6)
Os ₃ -O ₁₂ -C ₁₂			121.5(2.8)
O ₁₁ -Os ₂ -C ₅			100.8(1.5)
O ₁₂ -Os ₂ -C ₅			97.4(1.5)
O ₁₂ -Os ₂ -C ₆			95.0(1.4)
O ₁₁ -Os ₂ -C ₇			98.8(1.8)
O ₁₁ -Os ₃ -C ₈			96.7(1.7)
O ₁₂ -Os ₃ -C ₈			93.9(1.7)
O ₁₂ -Os ₃ -C ₉			96.5(1.7)
O ₁₁ -Os ₃ -C ₁₀			98.0(1.6)
Os ₂ -S ₁ -Os ₃		73.1(0.3)	
Os ₂ -S ₁ -C ₁₁		111.2(1.3)	

(to be continued)

TABLE 5 (continued)

Atoms	$\text{Os}_3(\text{CO})_{10}\text{H}_2$	$\text{Os}_3(\text{CO})_{10}\text{SC}_2\text{H}_3\text{H}$	$\text{Os}_3(\text{CO})_{10}(\text{OCH}_3)_2$
$\text{S}_1\text{—Os}_2\text{—C}_5$		92.7(1.7)	
$\text{S}_1\text{—Os}_2\text{—C}_7$		94.1(1.4)	
$\text{S}_1\text{—Os}_3\text{—C}_8$		97.3(1.3)	
$\text{S}_1\text{—Os}_3\text{—C}_{10}$		93.9(1.3)	
$\text{S}_1\text{—C}_{11}\text{—C}_{12}$		109.0(2.8)	
$\text{S}_1\text{—Os}_2\text{—Os}_5$		53.8(0.2)	
$\text{S}_1\text{—Os}_3\text{—Os}_2$		53.1(0.2)	

lengthening of the bonds $\text{Os}(1)\text{—Os}(2)$ and $\text{Os}(2)\text{—Os}(3)$ relative to the corresponding values in the other complexes and in $\text{Os}_3(\text{CO})_{12}$ [7]; no such effect is observed. But perhaps more conclusive evidence that the hydride ligands occupy bridging sites stems from the conformational arrangement of the carbonyl ligands in the three complexes, Fig. 1, 2 and 3 illustrate the close similarities in the overall molecular stereochemistries and we give a more quantitative discussion later. If, again, the hydride ligands were terminally bonding, the conformational relation between the three carbonyl ligands on each of $\text{Os}(2)$ and $\text{Os}(3)$ and the four carbonyl ligands on $\text{Os}(1)$ would approximate those in $\text{Os}_3(\text{CO})_{12}$, (Fig. 4) rather than that observed here.

The simple eighteen electron rule description of the metal—metal bonds has a counterpart in molecular orbital theory, either in a very simple form based entirely on symmetry considerations [8] or in a model [9] which, in principle at least, has claims to quantitiveness. An apparent difference between the two models is the symmetry attached to the highest orbitals in eighteen electron complexes although both are indicative that the polycentric orbital is antibonding with respect to the metals. The simple symmetry based model has some additional virtue in commenting directly not only on the geometries of polynuclear

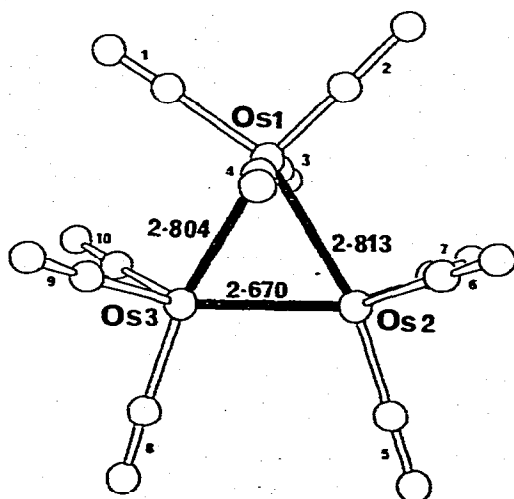


Fig. 1. $\text{H}_2\text{Os}_3(\text{CO})_{10}$: atomic arrangement and labelling. Carbonyl groups are labelled 1, 2 10 to include C1, O1; C2, O2 etc.

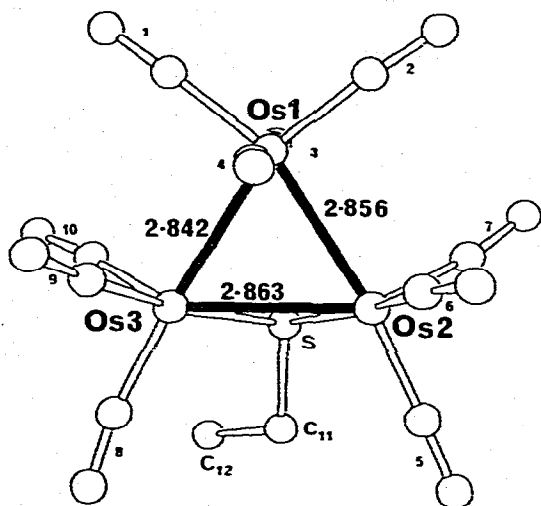


Fig. 2. $\text{H}(\text{SC}_2\text{H}_5)\text{Os}_3(\text{CO})_{10}$: atomic arrangement and labelling. The molecular perspective is essentially that depicted in Fig. 1.

complexes of non transition elements but also on the reasons for 'dihedrality' in bridged metal-metal bond frameworks [10]; a matter which has been discussed much more fully and recently by Burdett [11]. Dihedral angles between the planes containing Os(1) Os(2) Os(3) and Os(2) S Os(3) are 76° and 63° and 70° for the corresponding planes defined by the metal atoms and Os(2) O(11) Os(3) and Os(2) O(12) Os(3) respectively; it would be surprising if these values were not representative of the situation in $\text{H}_2\text{Os}_3(\text{CO})_{10}$ when it is defined by neutron diffraction studies.

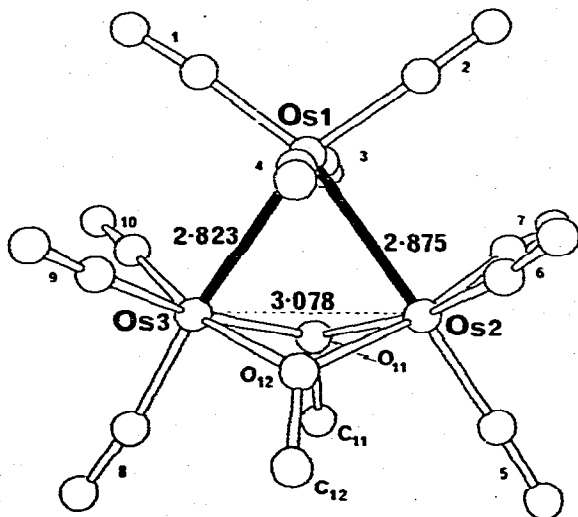


Fig. 3. $(\text{OCH}_3)_2\text{Os}_2(\text{CO})_{10}$: atomic arrangement and labelling. The molecular perspective is that of Fig. 1 and 2.

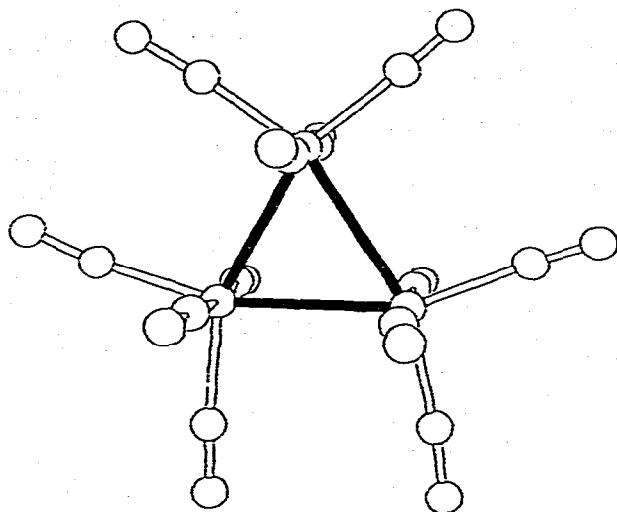


Fig. 4. The structure of $\text{Ru}_3(\text{CO})_{12}$ (and $\text{Os}_3(\text{CO})_{12}$) shown in essentially the same perspective, with respect to the metal framework, as in Fig. 1, 2 and 3.

TABLE 6

INTRAMOLECULAR CONTACTS (Å) RELATED TO THE QUESTION OF THE HYDRIDE ION POSITIONS IN $\text{H}_2\text{Os}_3(\text{CO})_{10}$

Molecule	Intramolecular atom pair contact				
$(\text{OCH}_3)_2\text{Os}(\text{CO})_{10}$	011...C3	2.77	} mean contact 2.98 Å		
	011...C5	3.18			
	011...C7	3.05			
	011...C8	2.96			
	011...C10	2.92			
	012...C4	2.88	} mean contact 2.93 Å		
	012...C5	3.01			
	012...C6	2.91			
	012...C8	2.92			
	012...C9	2.93			
		C1...C9	3.32	C3...C7	3.07
	C1...C10	3.19	C3...C10	3.06	
	C2...C6	3.26	C4...C6	3.02	
	C2...C7	3.17	C4...C9	3.08	
$\text{H}(\text{S}_2\text{C}_2\text{H}_5)\text{Os}_3(\text{CO})_{10}$	S...C3	2.98	} mean contact 3.14 Å		
	S...C5	3.11			
	S...C7	3.14			
	S...C8	3.29			
	S...C10	3.17			
		C1...C9	3.56	C3...C7	3.56
		C1...C10	3.49	C3...C10	3.29
	C2...C6	3.68	C4...C6	2.91	
	C2...C7	3.40	C4...C6	2.86	
$\text{H}_2\text{Os}_3(\text{CO})_{10}$	C1...C9	3.52	C3...C7	3.15	
	C1...C10	3.50	C3...C10	3.16	
	C2...C6	3.60	C4...C6	3.12	
	C2...C7	3.80	C4...C9	3.13	

Table 6 summarises, in our view, the reasons for being quite certain about the assignment of hydride ligands to symmetrical bridging positions, in other words for accepting the view that the three complexes are isostructural in the general sense of ligand distribution over the metal polyhedron. The contacts established between the oxygen and sulphur atoms of the μ -methoxy and -thiolato ligands and the carbonyl carbon atoms are very similar, the difference between mean contacts reflecting a small difference in van der Waals diameters. In the asymmetric complex, $\text{H}(\text{SEt})\text{Os}_3(\text{CO})_{10}$, the longer contact distances ($\text{C}(3)\dots\text{C}(7)$ and $\text{C}(3)\dots\text{C}(10)$) are again reflective of relative van der Waals diameters (vide $\text{C}(4)\dots\text{C}(6)$ and $\text{C}(4)\dots\text{C}(9)$). The carbonyl groups 6 and 7, together with 9 and 10, have in $\text{H}_2\text{Os}_3(\text{CO})_{10}$ 'leaned' towards the carbonyl ligands 2 and 1 compared with the situation in $(\text{OMe})_2\text{Os}_3(\text{CO})_{10}$ and, to a lesser extent, with that in $\text{H}(\text{SEt})\text{Os}_3(\text{CO})_{10}$. Again small steric effects between the bridging ligands and the axial carbonyl ligands, 3 and 4, are obvious from the results.

We have commented quantitatively [12] on the proposal that the structures of polynuclear carbonyls are determined by secondary valence forces between the carbonyl ligands [4]. It is pretty obvious that unless something even as simple as the one electron orbital energies for the metal-ligand bonds are taken into account, no structural model for the polynuclear carbonyls can have plausibility; it does seem that factorisation of the total energy into, on the one hand, the one electron molecular orbital energies and, on the other, secondary valence interactions could be adequate for discussing both the static and dynamic structures but convincing methodology is not to hand.

Acknowledgement

We are grateful to the S.R.C. for support.

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