

**CRYSTAL STRUCTURE OF A COMPLEX WITH A SUBSTITUTED
 METHYLENE LIGAND BOUND TO A TRIOSMIUM CLUSTER:
 $\text{Os}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CHSiMe}_3)$**

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Summary

The complex $\text{Os}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CHSiMe}_3)$ crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a 15.463(9), b 9.352(3), c 16.757(7) Å, β 107.38(4)°, V 2312.6(17) Å³ and $Z = 4$. Diffraction data (Mo- K_α , $2\theta(\text{max}) = 40^\circ$) were collected on a Syntex P2₁ diffractometer and the structure was refined to R_F 4.2% and R_{wF} 4.8% for all 2170 data (R_F 3.3%, R_{wF} 4.5% for those 1914 data with $|F_0| > 3\sigma(|F_0|)$). The molecule contains a triangular array of osmium atoms in which Os(2) and Os(3) are each associated with three terminal carbonyl ligands, while Os(1) is associated with four terminal carbonyls. Atoms Os(2) and Os(3) are mutually bridged by a nearly symmetrical bridging carbonyl ligand (Os(2)–C(1) 2.186(17) Å; Os(3)–C(1) 2.101(17) Å) and a bridging CHSiMe₃ ligand with Os(2)–C(2) 2.159(15) and Os(3)–C(2) 2.188(16) Å. The structure is an ordered analogue of the species $\text{Os}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CH}_2)$ which suffers from a four-fold disorder.

Introduction

Methylene groups have been implicated as key intermediates in Fischer-Tropsch [1–4] synthesis (eq. 1).



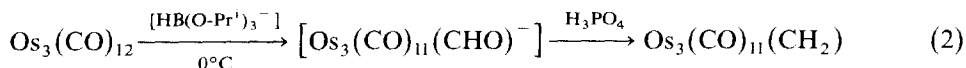
Brady and Pettit have shown [5,6] that surface-bound methylene groups, generated from diazomethane, couple (forming ethylene) in the absence of dihydrogen and generate hydrocarbon chains in the presence of dihydrogen.

Herrmann and his coworkers have carried out extensive studies on discrete

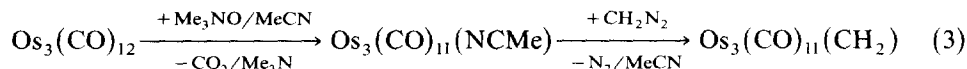
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molecular species containing bridging methylene groups; this work has recently been the subject of a review article [7].

The trinuclear osmium carbonyl methylene complex $\text{Os}_3(\text{CO})_{11}(\text{CH}_2)$ was originally prepared by Steinmetz and Geoffroy [8] as indicated by eq. 2.



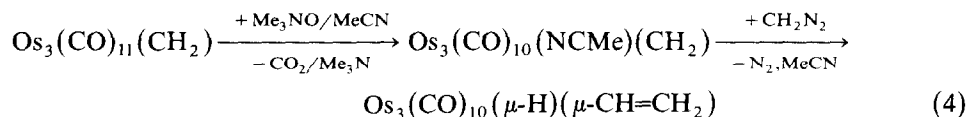
A second route to $\text{Os}_3(\text{CO})_{11}(\text{CH}_2)$ has been discovered by Shapley and coworkers [9] and is shown in eq. 3.



The complex $\text{Os}_3(\text{CO})_{11}(\text{CH}_2)$ is of considerable interest for the following reasons.

(1) It reacts with H_2 at 70–80°C yielding CH_4 and with D_2 yielding CH_2D_2 [8]. It is thus a good molecular model for the surface reaction of a CH_2 fragment with H_2 .

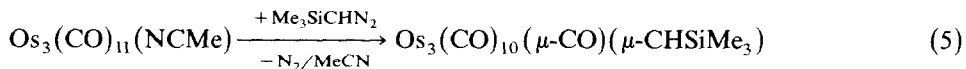
(2) A second methylene ligand can be introduced indirectly [9] yielding a hydrido-vinyl species by a coupling reaction (see eq. 4).



(3) Pyrolysis of $\text{Os}_3(\text{CO})_{11}(\text{CH}_2)$ at 80–110°C yields $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CCO})$ [10], a species in which a methylene and a carbonyl ligand have coupled. The reaction is believed to proceed via the asymmetric, “semi triply-bridging” methyldiyne complex $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-CH})$ [11].

Accurate crystal structures of the species $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{CCO})$ [12] and $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-CH})$ [11] have been completed. Unfortunately, a structural study of the starting material, $\text{Os}_3(\text{CO})_{11}(\text{CH}_2)$, showed it to suffer from a four-fold disorder [13]; although this species was found to have the stoichiometry $\text{Os}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CH}_2)$, accurate parameters are not available for the bridging ligands of interest.

However, the substituted methylene species, $\text{Os}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CHSiMe}_3)$, has been synthesized [9] as shown in eq. 5 and we have now completed a full three-dimensional X-ray structural analysis on this species.



Experimental section

Data collection. A small sample consisting of deep red plate-like crystals was kindly provided by Professor J.R. Shapley of the University of Illinois at Urbana-Champaign. A crystal trimmed to approximate dimensions of $0.25 \times 0.15 \times 0.075$ mm was mounted (in air) on a fiber and aligned on a Syntex P2₁ automated four-circle diffractometer. Crystal parameters and experimental data are summarized in Table I; a previous publication [14] has described the details of our operating procedures.

Data were corrected for Lorentz and polarization factors and for the effects of

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF $\text{Os}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CHSiMe}_3)$ *Crystal parameters*^a at 23(1)°C

Crystal system: Monoclinic	Space Group: $P2_1/n$
<i>a</i> 15.463(9) Å	<i>V</i> 2312.6(17) Å ³
<i>b</i> 9.352(3) Å	mol wt = 965.0
<i>c</i> 16.757(7) Å	ρ_{calc} 2.77 g cm ⁻³
β 107.38(4)°	<i>Z</i> = 4

*Data collection*Radiation: Mo- K_α ($\bar{\lambda}$ 0.710730 Å)Reflections measured: + *h*, + *k*, ± *l* 2θ range: 3.5–40°Scan type: θ (crystal)– 2θ (counter)Scan range: $[2\theta(K_{\alpha_1}) - 1.0]^\circ \rightarrow [2\theta(K_{\alpha_2}) + 1.0]^\circ$ Scan speed: 2.00° min⁻¹

Background measurement: Stationary crystal and counter at beginning and end of scan for a total of one-half total scan time

Standards: 600, 040, and 0,10,0 measured every 97 reflections; steady decay to approximately 96% initial intensity observed and corrected by application of an isotropic scaling factor

Reflections collected: 2303 total yielding 2170 independent

Absorption coefficient: 175.2 cm⁻¹^a Based on a least-squares refinement of setting angles of the unresolved Mo- K_α peaks of 15 reflections with 2θ 20–30°.

absorption and were converted to $|F_0|$ values. Any datum with a net intensity less than zero was assigned a value of $|F_0| = 0$.

Solution and refinement of the structure. The structure was solved via direct methods using the Syntex XTL version of the program MULTAN [15]. An “E-map” calculated using phases of 206 reflections with $E_{\text{min}} = 1.66$ provided the positions of the three independent osmium atoms and two subsequent difference-Fourier syntheses yielded all remaining nonhydrogen atoms. Full-matrix least-squares refinement minimizing $\sum w(\Delta F)^2$ was commenced using isotropic thermal parameters for the carbon atoms of the ten terminal carbonyl groups and anisotropic thermal parameters for all other nonhydrogen atoms. Hydrogen atoms in the >CHSiMe_3 ligand were included in fixed idealized positions with $d(\text{C-H})$ 0.95 Å [16] and were assigned B_{iso} 6.0 Å². A small correction for secondary extinction was made using the Zachariasen approximation in which $|F_{0,\text{cor}}| = |F_{0,\text{uncor}}|(1.0 + kI_0)$. The coefficient *k* was determined to be 1.13×10^{-7} by a least-squares fit of $|F_0|$ vs. $|F_c|$ for those 20 reflections with $I > 2 \times 10^5$. The final discrepancy factors were $R_F = (\sum |F_0| - |F_c|) / \sum |F_0| = 4.2\%$, $R_{wF} = [\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2]^{1/2} = 4.8\%$ and GOF = 1.03 for a model based on 221 variables refined against all 2170 unique data. The residuals based on those 1914 reflections satisfying $|F_0| > 3.0\sigma(|F_0|)$ were $R_F = 3.3\%$, $R_{wF} = 4.5\%$ and GOF = 1.03. Final positional and thermal parameters are listed in Tables 2 and 3.

TABLE 2

FINAL ATOMIC POSITIONAL PARAMETERS FOR $\text{Os}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CHSiMe}_3)$

Atom	x	y	z	B_{iso}
Os(1)	0.22377(4)	0.03928(7)	0.90041(4)	
Os(2)	0.16962(4)	0.32720(6)	0.91744(4)	
Os(3)	0.34439(4)	0.24419(6)	1.00281(4)	
Si	0.24195(35)	0.44982(51)	1.13114(30)	
C(1)	0.3003(11)	0.3863(19)	0.9017(11)	
O(1)	0.32507(79)	0.4611(14)	0.85367(79)	
C(2)	0.2326(10)	0.3063(16)	1.05052(92)	
C(3)	0.2811(15)	0.6315(21)	1.1051(12)	
C(4)	0.1263(16)	0.4718(24)	1.1424(14)	
C(5)	0.3188(16)	0.3858(24)	1.2313(11)	
C(11)	0.1179(12)	-0.0446(18)	0.8255(11)	4.45(37)
O(11)	0.0520(10)	-0.0919(17)	0.78162(94)	
C(12)	0.1856(12)	-0.0059(19)	0.9974(12)	4.70(38)
O(12)	0.16092(91)	-0.0324(13)	1.05263(83)	
C(13)	0.2697(11)	0.1147(20)	0.8093(12)	4.66(37)
O(13)	0.29559(89)	0.1548(13)	0.75886(71)	
C(14)	0.2995(11)	-0.1239(20)	0.9152(10)	4.57(36)
O(14)	0.3430(10)	-0.2260(13)	0.92704(85)	
C(21)	0.1409(10)	0.5238(19)	0.9251(10)	3.90(33)
O(21)	0.1180(10)	0.6449(13)	0.91969(92)	
C(22)	0.1185(12)	0.3213(18)	0.7978(12)	4.67(37)
O(22)	0.08635(90)	0.3250(17)	0.72662(80)	
C(23)	0.0630(14)	0.2564(20)	0.9360(12)	5.14(41)
O(23)	-0.00003(89)	0.2077(16)	0.9484(12)	
C(31)	0.4257(12)	0.3837(21)	1.0645(11)	5.09(39)
O(31)	0.4773(10)	0.4748(16)	1.09733(94)	
C(32)	0.4331(12)	0.1720(19)	0.9511(11)	4.75(38)
O(32)	0.48548(84)	0.1302(16)	0.92245(84)	
C(33)	0.3696(11)	0.1039(19)	1.0898(11)	4.40(35)
O(33)	0.3850(10)	0.0240(15)	1.14549(85)	
H(2)	0.2082	0.2538	1.0873	6.0
H(3A)	0.2836	0.6963	1.1493	6.0
H(3B)	0.2396	0.6662	1.0548	6.0
H(3C)	0.3395	0.6228	1.0979	6.0
H(4A)	0.1275	0.5437	1.1827	6.0
H(4B)	0.1071	0.3838	1.1600	6.0
H(4C)	0.0852	0.4989	1.0901	6.0
H(5A)	0.3244	0.4570	1.2729	6.0
H(5B)	0.3767	0.3664	1.2249	6.0
H(5C)	0.2949	0.3008	1.2476	6.0

Discussion

Interatomic distances and angles are collected in Tables 4 and 5. The scheme used for labeling atoms is illustrated in Fig. 1, while Fig. 2 provides a stereoscopic view of the molecule.

The crystal consists of discrete, ordered, $\text{Os}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CHSiMe}_3)$ molecules separated by normal Van der Waals' distances. The complex has approximate

TABLE 3

ANISOTROPIC THERMAL PARAMETERS FOR $\text{Os}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CHSiMe}_3)$ (in the form $\exp(-0.25(a^*h^2B_{11} + \dots + 2a^*b^*hkB_{12} + \dots))$)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	4.224(37)	2.751(33)	3.136(34)	-0.281(24)	1.012(26)	-0.145(24)
Os(2)	2.723(33)	3.174(36)	3.546(35)	0.311(22)	0.677(25)	0.203(24)
Os(3)	2.656(33)	3.607(37)	2.781(33)	0.379(23)	0.605(24)	-0.304(24)
Si	6.22(28)	4.34(25)	3.97(23)	0.20(20)	2.53(21)	-0.89(19)
C(1)	3.83(82)	3.91(84)	4.21(88)	0.97(70)	0.22(72)	-1.15(78)
O(1)	5.19(65)	6.67(75)	5.35(65)	-1.38(55)	1.86(54)	1.81(61)
C(2)	4.67(82)	3.31(73)	2.98(74)	1.17(65)	1.45(66)	-0.24(61)
C(3)	11.0(15)	4.0(10)	6.3(11)	0.55(95)	3.3(11)	-1.47(87)
C(4)	9.4(14)	8.6(14)	7.2(12)	1.2(12)	5.7(11)	-1.1(11)
C(5)	12.0(16)	7.1(12)	3.21(89)	0.7(12)	1.2(10)	-0.69(91)
O(11)	7.09(83)	8.83(92)	8.30(90)	-3.12(75)	-0.53(71)	1.15(79)
O(12)	8.80(82)	5.08(66)	6.68(72)	-1.09(58)	5.47(68)	-0.76(58)
O(13)	9.19(82)	5.45(68)	3.51(57)	-1.49(58)	2.79(60)	-0.61(51)
O(14)	8.54(85)	4.79(67)	6.92(80)	2.98(62)	2.07(66)	0.92(58)
O(21)	9.16(88)	3.80(65)	9.52(95)	2.11(59)	3.83(76)	2.10(62)
O(22)	6.53(75)	11.3(11)	3.79(66)	-0.73(71)	-0.18(56)	-0.12(67)
O(23)	4.58(69)	8.71(90)	14.9(14)	-2.19(67)	4.52(82)	0.76(94)
O(31)	7.38(79)	7.59(84)	8.79(92)	-3.37(69)	2.29(69)	-4.10(74)
O(32)	5.79(69)	9.62(92)	7.17(77)	1.89(66)	3.78(63)	-2.71(73)
O(33)	9.10(89)	7.87(83)	6.09(73)	3.58(72)	3.51(66)	3.36(68)

(non-crystallographically imposed) C_s (m) symmetry, both throughout the $\text{Os}_3(\text{CO})_{10}$ core and also within the bridging ligands.

The three osmium atoms define an isosceles triangle in which the ten terminal

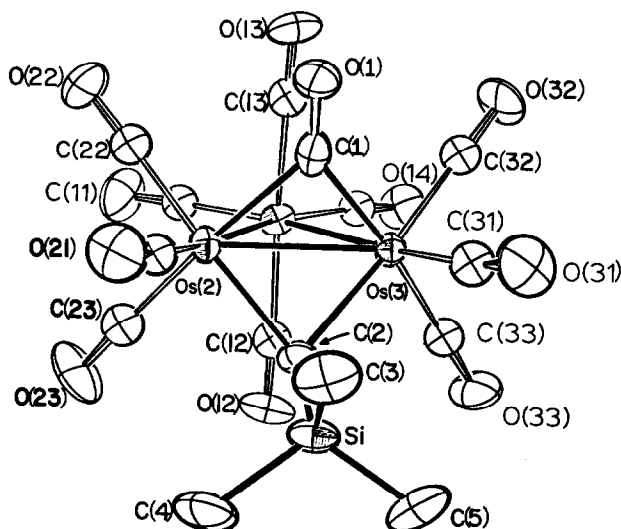


Fig. 1. Labelling of atoms in the $\text{Os}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CHSiMe}_3)$ molecule (ORTEP-II diagram; 30% ellipsoids).

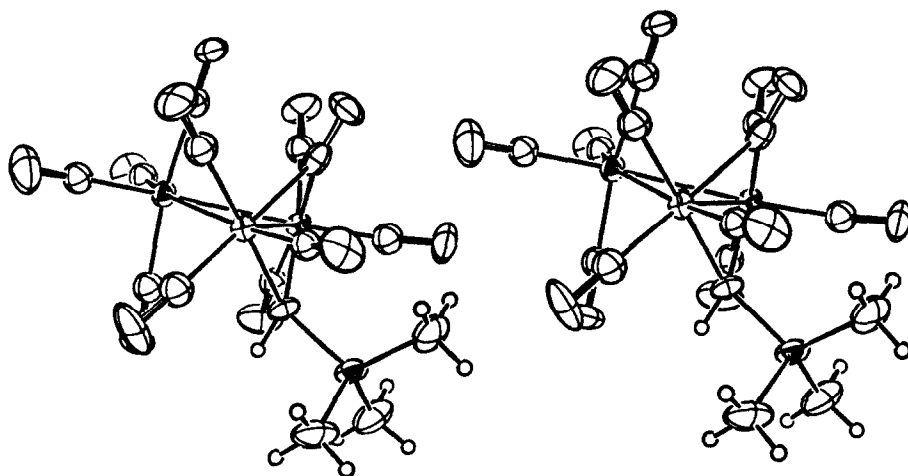


Fig. 2. Stereoscopic view of the $\text{Os}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CHSiMe}_3)$ molecule.

carbonyl ligands are distributed with three each associated with Os(2) and Os(3) and four associated with Os(1). The bond joining atoms Os(2) and Os(3) is bridged by a carbonyl ligand and a CHSiMe_3 moiety; the Os(2)–Os(3) distance of 2.765(1) Å is

TABLE 4

INTERATOMIC DISTANCES (Å) for $\text{Os}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CHSiMe}_3)$ with e.s.d.'s in parentheses

<i>Osmium – osmium distances</i>			
Os(1)–Os(2)	2.859(1)	Os(2)–Os(3)	2.765(1)
Os(1)–Os(3)	2.861(1)		
<i>Osmium – bridging ligand distances</i>			
Os(2)–C(1)	2.186(17)	Os(2)–C(2)	2.159(15)
Os(3)–C(1)	2.101(17)	Os(3)–C(2)	2.188(16)
<i>Osmium – carbonyl distances</i>			
Os(1)–C(11)	1.909(18)	Os(2)–C(22)	1.923(20)
Os(1)–C(12)	1.933(19)	Os(2)–C(23)	1.885(21)
Os(1)–C(13)	1.995(19)	Os(3)–C(31)	1.891(19)
Os(1)–C(14)	1.894(19)	Os(3)–C(32)	1.950(19)
Os(2)–C(21)	1.905(17)	Os(3)–C(33)	1.913(18)
<i>Terminal carbon – oxygen distances</i>			
C(11)–O(11)	1.153(24)	C(22)–O(22)	1.148(23)
C(12)–O(12)	1.130(23)	C(23)–O(23)	1.151(26)
C(13)–O(13)	1.104(22)	C(31)–O(31)	1.185(24)
C(14)–O(14)	1.151(23)	C(32)–O(32)	1.127(24)
C(21)–O(21)	1.182(21)	C(33)–O(33)	1.163(22)
<i>Bridging carbon – oxygen distance</i>			
C(1)–O(1)	1.211(22)		
<i>Distances within the $\mu\text{-CHSiMe}_3$ ligand</i>			
C(2)–Si	1.879(16)	Si–C(4)	1.864(26)
Si–C(3)	1.898(21)	Si–C(5)	1.843(20)

TABLE 5

INTERATOMIC ANGLES (DEG) FOR $\text{Os}_3(\text{CO})_{10}(\mu\text{-CO})(\mu\text{-CHSiMe}_3)$ with e.s.d.'s in parentheses*Osmium – osmium – osmium angles*

Os(3)–Os(1)–Os(2)	57.81(2)	Os(2)–Os(3)–Os(1)	61.07(2)
Os(1)–Os(2)–Os(3)	61.12(2)		

Angles involving the bridging ligands

Os(2)–C(1)–Os(3)	80.3(6)	Os(2)–C(2)–Os(3)	79.0(5)
C(1)–Os(2)–Os(3)	48.5(5)	C(2)–Os(2)–Os(3)	51.0(4)
C(1)–Os(3)–Os(2)	51.2(5)	C(2)–Os(3)–Os(2)	50.0(4)
C(1)–Os(2)–C(21)	90.4(7)	C(2)–Os(2)–C(21)	93.5(7)
C(1)–Os(2)–C(22)	89.3(7)	C(2)–Os(2)–C(22)	172.7(7)
C(1)–Os(2)–C(23)	173.5(8)	C(2)–Os(2)–C(23)	86.9(7)
C(1)–Os(2)–Os(1)	85.2(5)	C(2)–Os(2)–Os(1)	87.8(4)
C(1)–Os(3)–Os(1)	86.8(8)	C(2)–Os(3)–Os(1)	87.3(4)
C(1)–Os(3)–C(31)	90.4(8)	C(2)–Os(3)–C(31)	96.0(5)
C(1)–Os(3)–C(32)	87.8(7)	C(2)–Os(3)–C(32)	173.0(5)
C(1)–Os(3)–C(33)	172.7(7)	C(2)–Os(3)–C(33)	84.7(7)
C(1)–Os(2)–C(2)	90.0(6)	C(1)–Os(3)–C(2)	91.5(6)

Osmium – osmium – carbonyl angles

Os(2)–Os(1)–C(11)	103.5(5)	Os(3)–Os(1)–C(11)	161.3(5)
Os(2)–Os(1)–C(12)	87.1(5)	Os(3)–Os(1)–C(12)	87.1(5)
Os(2)–Os(1)–C(13)	85.7(5)	Os(3)–Os(1)–C(13)	84.5(5)
Os(2)–Os(1)–C(14)	159.0(5)	Os(3)–Os(1)–C(14)	101.2(5)
Os(1)–Os(2)–C(21)	175.4(5)	Os(1)–Os(3)–C(31)	176.5(6)
Os(1)–Os(2)–C(22)	84.9(5)	Os(1)–Os(3)–C(32)	85.5(5)
Os(1)–Os(2)–C(23)	89.0(6)	Os(1)–Os(3)–C(33)	86.9(5)
Os(3)–Os(2)–C(21)	116.6(5)	Os(2)–Os(3)–C(31)	118.5(6)
Os(3)–Os(2)–C(22)	124.4(6)	Os(2)–Os(3)–C(32)	125.2(6)
Os(3)–Os(2)–C(23)	125.7(6)	Os(2)–Os(3)–C(33)	122.2(5)

Carbonyl – osmium – carbonyl angles

C(11)–Os(1)–C(12)	92.6(8)	C(21)–Os(2)–C(22)	93.8(8)
C(11)–Os(1)–C(13)	94.2(8)	C(21)–Os(2)–C(23)	95.4(8)
C(11)–Os(1)–C(14)	97.5(8)	C(22)–Os(2)–C(23)	93.1(8)
C(12)–Os(1)–C(13)	171.1(8)	C(31)–Os(3)–C(32)	92.3(8)
C(12)–Os(1)–C(14)	92.6(8)	C(31)–Os(3)–C(33)	96.1(8)
C(13)–Os(1)–C(14)	92.1(8)	C(32)–Os(3)–C(33)	95.2(8)

Osmium – carbon – oxygen angles

Os(1)–C(11)–O(11)	177.4(16)	Os(2)–C(22)–O(22)	176.4(16)
Os(1)–C(12)–O(12)	178.1(16)	Os(2)–C(23)–O(23)	177.0(18)
Os(1)–C(13)–O(13)	179.1(16)	Os(3)–C(31)–O(31)	174.8(17)
Os(1)–C(14)–O(14)	176.2(16)	Os(3)–C(32)–O(32)	178.8(17)
Os(2)–C(21)–O(21)	172.0(15)	Os(3)–C(33)–O(33)	176.6(16)

Angles within the bridging ligands

Os(2)–C(1)–O(1)	135.5(13)	Os(3)–C(1)–O(1)	144.2(14)
Os(2)–C(2)–Si	126.3(8)	Os(3)–C(2)–Si	123.6(8)
C(2)–Si–C(3)	115.8(8)	C(3)–Si–C(4)	107.8(10)
C(2)–Si–C(4)	106.3(9)	C(3)–Si–C(5)	109.7(10)
C(2)–Si–C(5)	108.2(9)	C(4)–Si–C(5)	108.7(10)

thus substantially shorter than the non-bridged distances, viz., Os(1)–Os(2) 2.859(1) and Os(1)–Os(3) 2.861(1) Å.

The difference between the average non-bridged distance and the doubly bridged osmium–osmium distance is 0.095 Å which is very close to the corresponding value of 0.089 Å determined for Os₃(CO)₁₀(μ-CO)(μ-CH₂). In this latter parent species (which suffers from disorder) all metal–metal bond lengths were slightly smaller; the dibridged vector was reduced to 2.749(2) Å while the nonbridged distances were 2.833(2) and 2.844(2) Å [13]. A similar trend between bridged and non-bridged distances was found in Fe₃(CO)₁₀(μ-CO)₂ [17,18], with which Os₃(CO)₁₀(μ-CO)(μ-CH₂) is isomorphous.

Both bridging ligands in the Os₃(CO)₁₀(μ-CO)(μ-CHSiMe₃) molecule span the Os(2)–Os(3) vector nearly symmetrically. The osmium–(μ-methylidene) distances are Os(2)–C(2) 2.159(15) and Os(3)–C(2) 2.188(16) Å; the difference of 0.029 ± 0.022 Å is significant only at the 1.3σ level.

Although disorder problems made it impossible to determine accurately the Os–(μ-CH₂) distances in Os₃(CO)₁₀(μ-CO)(μ-CH₂) [13], there have been measurements on some 1,3-dipolar μ-hydrido-μ-carbene complexes of the triosmium framework. Osmium–(μ-carbene) distances of 2.148(9) and 2.173(8) were found in (μ-H)Os₃(CO)₁₀(μ- $\bar{C}HCH_2PMe_2Ph$) [19], while Os–(μ-CHCH=NEt₂) distances of 2.15(3) and 2.16(3) Å were found in (μ-H)Os₃(CO)₁₀(μ- $\bar{C}HCH=NEt_2$) [20]. These distances are thus consistent with those found in Os₃(CO)₁₀(μ-CO)(μ-CHSiMe₃).

The present molecule also possesses a μ₂-bridging carbonyl ligand in which Os(2)–C(1) 2.186(17) and Os(3)–C(1) 2.101(17) Å (the difference of 0.085 ± 0.024 Å represents ca. 3.5σ). Despite this slight asymmetry, this molecule is the clearest example of a triosmium complex possessing a bridging carbonyl ligand. We assume that Os₃(CO)₁₀(μ-CO)(μ-CH₂) has a symmetrical Os(μ-CO)Os bridge. The only other triosmium derivative known to have bridging carbonyl ligands is Os₃(CO)₁₀(PhC₂Ph) [21]; here, however, the bridges are clearly unsymmetrical and of the “semi-bridging” variety. (Distances of note in this structure are Os(1)–C(2) 1.944(12) vs. Os(3) ··· C(2) 2.765(10) Å and Os(1)–C(4) 1.961(9) vs. Os(2) ··· C(4) 2.745(8) Å.)

In the present molecule the triosmium plane makes dihedral angles of 113.06° (66.94°) with the Os(2)–C(2)–Os(3) plane and 111.18° (68.82°) with the Os(2)–C(1)–Os(3) plane; the dihedral angle between the bridging methylidene and carbonyl ligands (i.e., Os(2)–C(2)–Os(3)/Os(2)–C(1)–Os(3)) is 135.75° (44.25°). The overall molecular skeleton of Os₃(CO)₁₀(μ-CO)(μ-CHSiMe₃) is thus very similar to that found in a variety of (μ-H)Os₃(CO)₁₀(μ-L) complexes [22].

All other distances and angles in the molecule lie within their expected ranges (cf. Tables 4 and 5).

Additional data. See NAPS document no. 04076 for 12 pages of Supplementary Material (list of observed and calculated structure factor amplitudes). Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance in U.S. funds only \$7.75 for photocopies or \$4.00 for microfiche. Outside the U.S. and Canada add postage of \$4.50 for the first 20 pages and \$1.00 for each page thereafter. \$1.50 for microfiche postage.

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