Synthesis and Molecular Structures of New Silylalkyne Triosmium Clusters†

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Treatment of the functionalized cluster $[Os_3(CO)_{10}(MeCN)_2]$ with trimethylsilylacetylene quantitatively affords $[Os_3(CO)_{10}(HCCSiMe_3)]$ **1** which in refluxing heptane undergoes decarbonylation and hydrogen migration yielding $[Os_3H(CO)_9(CCSiMe_3)]$ **2** the structure of which was determined by an X-ray study [triclinic, space group $P\bar{1}$, $a = 9.201(2)$, $b = 13.127(2)$, $c = 9.118(7)$ Å, $\alpha = 107.31(3)$, $\beta = 98.57(3)$, $\gamma = 93.18(2)°$, $Z = 2$]. Desilylation of **2** affording $[Os_3H(CO)_9(C_2H)]$ takes place either on silica TLC plates or on stirring in hot methanol. The compound $[Os_3H(CO)_{10}(CCSiMe_3)]$ **3** has been prepared through two different routes: (*i*) reaction of $[Os_3H(CO)_{10}Cl]$ with $Li[C{\equiv}CSiMe_3]$; (*ii*) reaction of $[Os_3(CO)_{11}(MeCN)]$ with $HCCSiMe_3$. It has been characterized by X-ray diffraction studies [monoclinic, space group $P2_1/c$, $a = 13.338(5)$, $b = 9.141(4)$, $c = 18.902(7)$ Å, $\beta = 109.99(3)°$, $Z = 4$]. On refluxing **3** in heptane, decarbonylation occurs with formation of **2**.

The chemistry and reactivity of unsaturated hydrocarbyl ligands co-ordinated to several metal atom centres has attracted considerable interest[1] since these systems may provide good models for the chemisorption of small hydrocarbon molecules on metal surfaces.[2] The synthetic route to the synthesis of alkyne-substituted metal clusters is now well established. The use of lightly co-ordinated ligands in cluster chemistry has proved to be a general procedure for high-yield synthesis of a wide variety of alkyne clusters without the plethora of by-products commonly found in the thermal activation of binary carbonyl clusters.[3] Within the family of triosmium clusters three co-ordination modes of the alkyne on the metal framework have been observed and structurally characterized: (*a*) μ_3-η^2 (∥); (*b*) μ_3-η^2 (⊥); and (*c*) μ-η^2 (see Fig. 1). The most common bonding mode, *i.e.* (*a*) has been found in clusters of general formula $[Os_3(CO)_{10}(R^1C_2R^2)]$ ($R^1 = R^2 = Et$;[4] $R^1 = H$, R^2 = ferrocenyl[5]) and $[M_3H_2(CO)_9(R_2C_2)]$ (M = Ru, R = H, Me or Et, M = Os, R = H, Me or Ph).[6,7] Mode (*b*) has been observed in $[Os_3(CO)_7(Ph_2PCH_2PPh_2)(Ph_2C_2)]$,[8] $[Os_3(\mu\text{-}H)(C_2R)(CO)_9]$ (R = ferrocenyl)[5] and $[Os_3(\mu\text{-}H)(CCCF_3)(CO)_9]$.[9] Finally the less-common mode (*c*) has been observed in $[Os_3(C{\equiv}CPh)\{Au(PMe_2Ph)\}(CO)_{10}]$[10] and $[Os_3H(CO)_9L(\mu\text{-}\eta^2\text{-}C{\equiv}CPh)]$ (L = CO or PMe_2Ph).[11]

As a part of our objective to prepare organometallic polymers we became interested in the synthesis of alkyne-substituted triosmium clusters in which the alkyne unit adopts different co-ordination modes with the aim to prepare suitable precursors to linked osmium cluster systems. Here we report the synthesis of such clusters which exhibit three co-ordination modes characterized by spectroscopy and X-ray diffraction studies for two of them. Some aspects of this work have been communicated previously.[12]

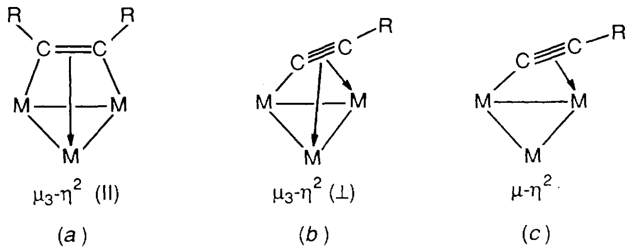

Fig. 1 Bonding modes of alkyne ligands in triosmium clusters

Results and Discussion

Synthesis of $[Os_3(CO)_{10}(HCCSiMe_3)]$.—The bis(acetonitrile) derivative $[Os_3(CO)_{10}(MeCN)_2]$ reacts smoothly with the terminal acetylene $HCCSiMe_3$ in CH_2Cl_2 solution at room temperature to afford in a few minutes the cluster $[Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}HCCSiMe_3)]$ **1** (see Scheme 1) which has been characterized on the basis of IR and ^1H NMR spectroscopy (see Table 1). The IR band pattern in the ν_{CO} region is strictly comparable to that found for other similar $[Os_3(CO)_{10}(C_2R_2)]$ derivatives.[7] An absorption band at 1854 cm^{-1} in hexane solution is indicative of the presence of a bridging carbonyl ligand. The ^1H NMR spectrum of **1** in $CDCl_3$ shows a low-field signal at δ 10.53 in the range expected for a ≡CH proton in a similar environment, in addition to a singlet attributable to the nine hydrogen atoms of the trimethylsilyl group. The close similarity of its spectroscopic properties to those of already known compounds of the type $[Os_3(CO)_{10}(alkyne)]$[7] provides good evidence in support of its formulation as $[Os_3(CO)_{10}(HCCSiMe_3)]$. Further evidence of the co-ordination mode μ_3-η^2 (∥) of the alkyne ligand in this class of compounds has been recently gained from crystal structure studies on $[Os_3(CO)_{10}(EtCCEt)]$[4] and $[Os_3(CO)_{10}(HCCR)]$ (R = ferrocenyl).[5] Although the reaction was carried out with excess of alkyne, formation of by-products derived by alkyne coupling on the metal framework was not observed probably because of the mild conditions.

Thermolysis of $[Os_3(CO)_{10}(HCCSiMe_3)]$ **1**.—The orange compound **1** slowly decarbonylates in CH_2Cl_2 solution or even in the solid state at room temperature to afford the off-white cluster $[Os_3(\mu\text{-}H)(CO)_9(CCSiMe_3)]$ **2**. Complete conversion was effected by heating at reflux a solution of $[Os_3(CO)_{10}$-

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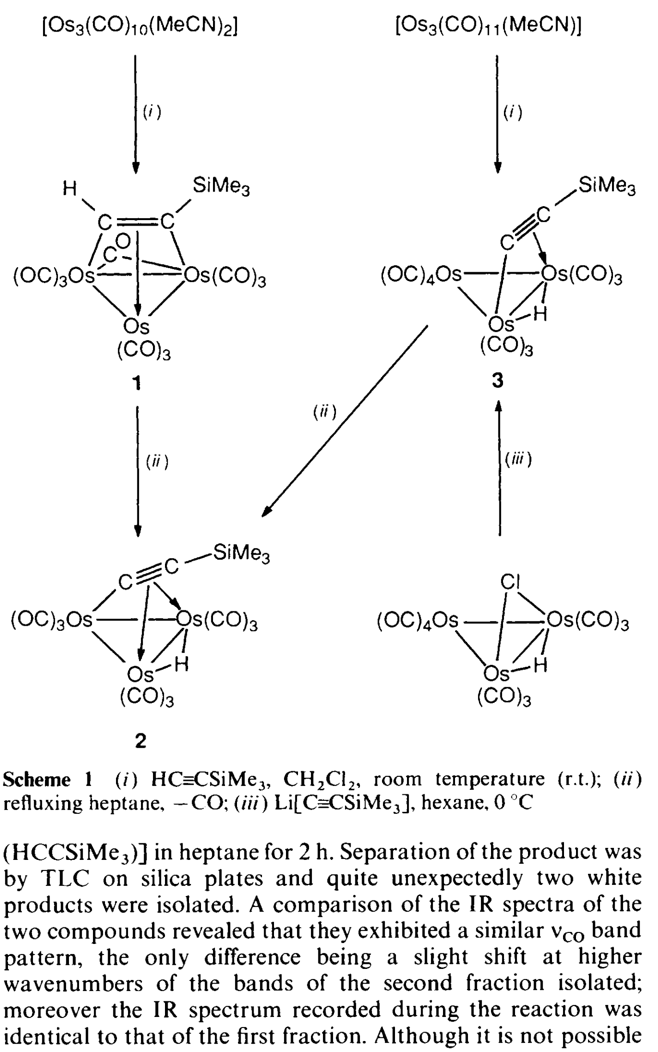
† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Spectroscopic data for the new complexes

Compound	IR (ν_{CO}[a]/cm^{-1})	^{1}H NMR[b] (δ)	*m/z*[c]
1 $[Os_3(CO)_{10}(HCCSiMe_3)]$	2099m, 2059vs, 2056vs(sh), 2023vs, 2008s, 1999s, 1854m	10.53 (s, 1 H), 0.040 (s, 9 H)	954
2 $[Os_3H(CO)_9(CCSiMe_3)]$	2100w, 2074s, 2052s, 2020vs, 2011s, 1981m, 1949w	0.38 (s, 9 H), −23.70 (s, 1 H)	926
3 $[Os_3H(CO)_{10}(CCSiMe_3)]$	2111w, 2069vs, 2062s, 2026vs, 2020s, 2005s, 1992w, 1984m, 1951w	0.29 (s, 9 H), −16.92 (s, 1 H)	954

[a] In hexane. [b] In $CDCl_3$. [c] Molecular ion (M^+) based on ^{192}Os.



Scheme 1 (*i*) $HC{\equiv}CSiMe_3$, CH_2Cl_2, room temperature (r.t.); (*ii*) refluxing heptane, −CO; (*iii*) $Li[C{\equiv}CSiMe_3]$, hexane, 0 °C

$(HCCSiMe_3)]$ in heptane for 2 h. Separation of the product was by TLC on silica plates and quite unexpectedly two white products were isolated. A comparison of the IR spectra of the two compounds revealed that they exhibited a similar ν_{CO} band pattern, the only difference being a slight shift at higher wavenumbers of the bands of the second fraction isolated; moreover the IR spectrum recorded during the reaction was identical to that of the first fraction. Although it is not possible to rule out the formation in low yields of the second product during the thermolysis of compound **1**, some reaction must have occurred during chromatographic work-up of the reaction mixture. Our hypothesis is also strengthened by the findings of other research groups who separated reaction products by using chromatographic techniques. For example, the heteronuclear alkyne-substituted cluster $[Co_2Fe(CO)_9(RCCSiMe_3)]$ has been reported to undergo desilylation on a silica column to afford $[Co_2Fe(CO)_9(MeCCH)]$,[13] and $[Fe(\mu\text{-}H)(CO)_9(C{\equiv}CSiMe_3)]$ has been isolated after column chromatography on alumina from the low-temperature reaction of bis(trimethylsilyl)-acetylene, $[Fe(CO)_5]$ and vaporized nickel atoms.[14] Also in the latter case hydrolytic cleavage of a C–Si bond has been proposed in order to account for the loss of one trimethylsilyl group. In order to find out if the behaviour of compound **2** on silica was reproducible, the compound was stirred in methanolic solution at 65 °C for 5 h to give almost quantitatively a pale white compound whose IR spectrum was identical to that of the second fraction isolated after thermolysis of compound **1**.

Compound **2** was characterized by IR, ^{1}H and ^{13}C NMR and mass spectroscopy. The IR spectrum in the ν_{CO} region resembles that of clusters of formula $[Os_3(\mu\text{-}H)(CO)_9(CCR)]$.[7] The presence of an hydride is confirmed by the signal at δ −23.70 whereas the trimethylsilyl protons resonate at δ 0.38. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum the two acetylenic carbon atoms show a downfield shift at δ 144.27 and an upfield shift at δ 48.71, respectively, consistent with values reported for other $\mu_3\text{-}\eta^2$ (⊥) acetylide clusters of this type.[15] An X-ray structural determination was carried out on compound **2** (see below). The desilylated cluster $[Os_3(\mu\text{-}H)(CO)_9(CCH)]$ was characterized by comparison of its spectroscopic properties with those reported in the literature.[7,16]

Synthesis of $[Os_3H(CO)_{10}(CCSiMe_3)]$ **3**.—It is well known that one of the methods for the synthesis of transition-metal acetylide complexes is the reaction of sodium or lithium acetylides with metal carbonyls or metal halides.[17] This synthetic approach has recently been used also for preparation of the cluster compounds $[Os_3(\mu\text{-}H)(CO)_9L(C{\equiv}CPh)]$ (L = CO or PMe_2Ph) by treating the acetylide $Li[C{\equiv}CPh]$ with $[Os_3(\mu\text{-}H)(CO)_9L(Cl)]$.[11] The acetylide $[C{\equiv}CPh]^-$, which behaves as a three-electron donor replacing the bridging chloride, bridges asymmetrically the hydride-bridged Os–Os bond, being σ-bound to one metal and π-bound to the other ($\mu\text{-}\eta^2$ bonding mode). Since we were investigating the different co-ordination modes which can be adopted by a terminal acetylene or acetylide containing the trimethylsilyl group as substituent and being aware of the role of the substituent on the acetylene in driving the reaction towards different products, we treated $[Os_3H(CO)_{10}Cl]$ with $Li[C{\equiv}CSiMe_3]$. The reaction carried out at 0 °C in hexane under N_2 afforded the triosmium cluster $[Os_3(\mu\text{-}H)(CO)_{10}(CCSiMe_3)]$ **3**, characterized on the basis of IR, ^{1}H NMR and mass spectroscopy. The IR spectrum closely resembles that of other complexes of the general type $[Os_3(\mu\text{-}H)(CO)_{10}(C{\equiv}CR)]$.[7] In the ^{1}H NMR spectrum a resonance at δ −16.92 in the range of hydridic hydrogens is seen in addition to the singlet signal of the $SiMe_3$ hydrogens at δ 0.29. A parent-ion peak at *m/z* 954 (^{192}Os) in the mass spectrum is consistent with the proposed formulation. Although the $\mu\text{-}\eta^2$ co-ordination mode is very common for binuclear transition-metal complexes it is quite rare in trinuclear clusters. For this reason orange crystals of $[Os_3(\mu\text{-}H)(CO)_{10}(C{\equiv}CSiMe_3)]$ suitable for an X-ray single-crystal study were grown from pentane solutions at −20 °C in order to elucidate this co-ordination mode.

Alternative Synthesis of Compound **3**.—The reaction of $[Os_3(CO)_{11}(MeCN)]$ with ethylene leads to the formation of the stable compound $[Os_3(CO)_{11}(C_2H_4)]$ in which the alkene ligand is 'side-on' bonded to one osmium atom,[18] whereas with acetylene in 'wet' CH_2Cl_2 a high yield of $[Os_3(CO)_9(C_3H_2OH)H]$[19] is obtained. The latter contains an allyl alcohol, probably originating from one molecule of acetylene and one CO ligand, which is co-ordinated to the three metal atoms *via* two σ bonds and a π-allyl bond. The alkyne-substituted cluster $[Os_3(CO)_{10}(C_2H_2)]$ was isolated from the same reaction only as a minor by-product. When trimethylsilylacetylene was treated at room temperature with $[Os_3(CO)_{11}(MeCN)]$ in 'dry' CH_2Cl_2 a yellow-orange product was formed in high yield (60%). Characterization of this product by IR, ^{1}H NMR and mass spectroscopy revealed that also in this reaction $[Os_3H(CO)_{10}(C{\equiv}CSiMe_3)]$ was formed instead of the simple sub-

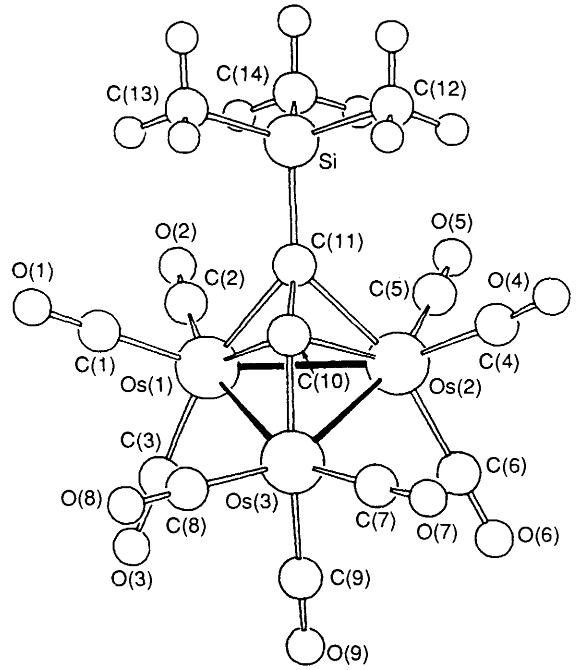


Fig. 2 Molecular structure of [$Os_3H(CO)_9(CCSiMe_3)$] **2** showing the atom numbering scheme

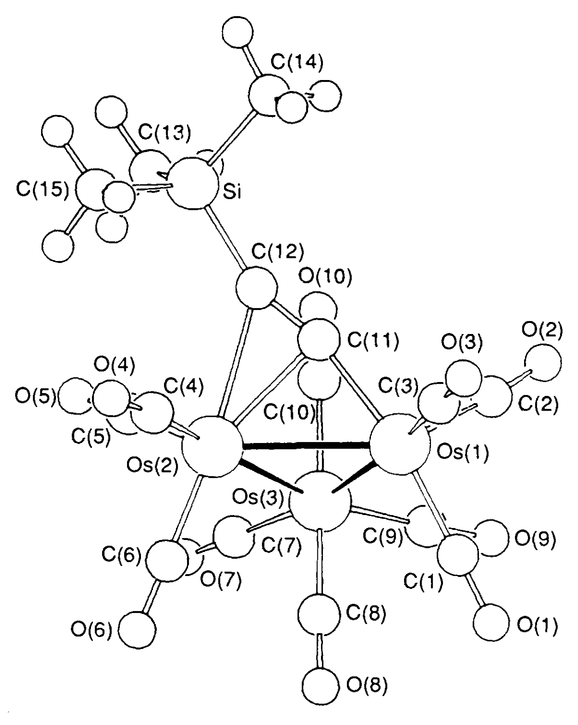


Fig. 3 Molecular structure of [$Os_3H(CO)_{10}(CCSiMe_3)$] **3** showing the atom numbering scheme

stitution product [$Os_3(CO)_{11}(HCCSiMe_3)$]. This apparently unexpected result is justified in terms of maximized back donation achieved by co-ordination of the alkyne to more than one metal centre. Although the cluster [$Os_3(CO)_{11}(HCCSiMe_3)$] could not be isolated it seems reasonable to put forward a reaction mechanism analogous to that found for the reaction of [$Os_3(CO)_{11}(MeCN)$] with terminal alkenes. In our case [$Os_3(CO)_{11}(HCCSiMe_3)$] would be an intermediate product which undergoes CO loss and hydrogen migration on the metal core to afford eventually [$Os_3H(CO)_{10}(CCSiMe_3)$] **3**. Upon refluxing **3** in heptane for 6 h, again conversion into [$Os_3H(CO)_9(CCSiMe_3)$] is observed.

Table 2 Selected bond lengths (Å) and angles (°) for compound **2**

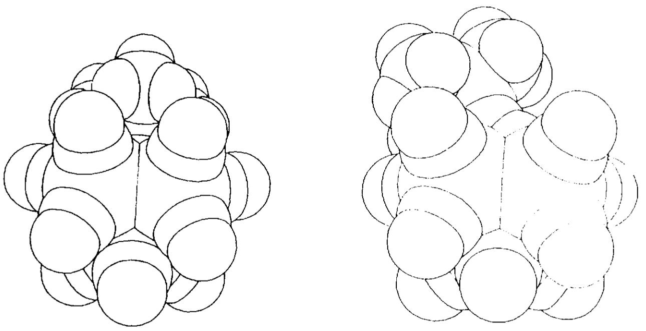
Os(1)–Os(2)	2.833(1)	Os(3)–C(10)	1.94(1)
Os(1)–Os(3)	2.846(1)	C(10)–C(11)	1.31(1)
Os(2)–Os(3)	2.843(1)	C(11)–Si	1.87(1)
Os(1)–C(1)	1.89(1)	C(12)–Si	1.84(1)
Os(1)–C(2)	1.93(1)	C(13)–Si	1.84(1)
Os(1)–C(3)	1.89(1)	C(14)–Si	1.84(1)
Os(1)–C(10)	2.23(1)	C(1)–O(1)	1.16(1)
Os(1)–C(11)	2.26(1)	C(2)–O(2)	1.13(1)
Os(2)–C(4)	1.90(1)	C(3)–O(3)	1.15(1)
Os(2)–C(5)	1.92(1)	C(4)–O(4)	1.15(1)
Os(2)–C(6)	1.89(1)	C(5)–O(5)	1.14(1)
Os(2)–C(10)	2.23(1)	C(6)–O(6)	1.16(1)
Os(2)–C(11)	2.25(1)	C(7)–O(7)	1.13(1)
Os(3)–C(7)	1.90(1)	C(8)–O(8)	1.13(1)
Os(3)–C(8)	1.91(1)	C(9)–O(9)	1.15(1)
Os(3)–C(9)	1.91(1)		
Os(1)–Os(2)–Os(3)	60.2(1)	C(12)–Si–C(14)	110(1)
Os(2)–Os(1)–Os(3)	60.1(1)	C(11)–Si–C(14)	110.2(5)
Os(1)–Os(3)–Os(2)	59.7(1)	C(1)–Os(1)–C(2)	93.1(4)
Os(3)–C(10)–C(11)	154(1)	C(1)–Os(1)–C(3)	91.4(4)
C(10)–C(11)–Si	140(1)	C(2)–Os(1)–C(3)	99.2(4)
C(11)–Os(1)–Os(2)	51.0(2)	C(4)–Os(2)–C(5)	94.0(5)
Os(1)–C(11)–Os(2)	77.8(3)	C(4)–Os(2)–C(6)	91.9(4)
C(11)–Os(2)–Os(1)	51.2(2)	C(5)–Os(2)–C(6)	99.5(5)
C(11)–C(10)–Os(1)	74.3(5)	C(7)–Os(3)–C(8)	95.8(5)
C(11)–C(10)–Os(2)	73.8(5)	C(7)–Os(3)–C(9)	94.8(5)
Os(1)–C(10)–C(11)	74.3(5)	C(8)–Os(3)–C(9)	94.1(5)
Os(2)–C(10)–C(11)	73.8(5)	Os(1)–Os(2)–C(6)	115.8(3)
Os(3)–C(10)–Os(2)	85.6(3)	Os(2)–Os(1)–C(3)	116.1(3)
Os(1)–C(10)–Os(3)	85.9(3)	Os(2)–Os(3)–C(9)	100.1(3)
Si–C(11)–Os(1)	134.5(5)	Os(1)–Os(3)–C(9)	99.8(4)
Si–C(11)–Os(2)	133.7(4)	Os(2)–Os(1)–C(2)	103.4(3)
C(11)–Si–C(13)	107.9(5)	Os(1)–Os(2)–C(5)	102.4(3)
C(11)–Si–C(12)	107(1)	Os(1)–Os(3)–C(8)	99.5(3)
C(12)–Si–C(13)	111(1)	Os(2)–Os(3)–C(7)	101.6(3)
C(13)–Si–C(14)	111(1)		

Structural Characterization of Compounds **2** *and* **3**.—The structures of the trinuclear complexes **2** and **3** are shown in Figs. 2 and 3, respectively. The two molecules are closely related and will be discussed together in the following section. Relevant structural parameters are reported in Tables 2 and 3. The two species differ in the number of CO ligands (nine in **2**, ten in **3**) and in the co-ordination mode adopted by the $C{\equiv}CSiMe_3$ ligand. In **2** this ligand is bound to the metal framework in μ_3-η^2 ($\perp$) fashion with the triple bond perpendicular to one Os–Os bond of the almost equilateral Os_3 triangle [Os–Os ranging from 2.833(1) to 2.846(1) Å]. The nine CO groups are distributed three on each Os atom. In **3** the $C{\equiv}CSiMe_3$ ligand is bound in μ-η^2 fashion over an edge of the Os_3 triangle [Os–Os 2.836(1)–2.861(1) Å]. The two Os atoms involved in the bridge also bear three CO groups each, while four CO groups are terminally bound to the remaining Os. In such a way, and according to the usual electron-counting rules, the $C{\equiv}CSiMe_3$ ligand is required to supply five electrons to the metal cluster orbitals in **2** (*via* 2π and 1σ interaction) and three electrons in **3** (*via* one σ and one π interaction). The difference in length between the two $C{\equiv}C$ systems [1.31(1) in **2**, against 1.24(2) Å in **3**] is in agreement with this picture of the bonding interactions. It is interesting that the deviation from linearity of the whole Os–C(11)–C(12)–Si system in **3** is very small [Os(1)–C(11)–C(12) 167(1), C(11)–C(12)–Si 162(1)°] considering the strain imposed upon the system by its bonding mode. As expected the two Os–C_π distances in **3** are not equivalent [2.32(1) *versus* 2.53(1) Å] and appear to be longer than in **2** [Os–C_π 2.23(1)–2.26(1) Å]. The Os–C_σ interaction is also longer in **3** [2.02(1) Å] than in **2** [1.94(1) Å]. In the latter case, however, the deformations of the Os–C≡C–SiMe$_3$ ligand are larger [Os(3)–C(10)–C(11) 154(1), C(10)–C(11)–Si 140(1)°] indicating that the

Table 3 Selected bond lengths (Å) and angles (°) for compound **3**

Os(1)–Os(2)	2.861(1)	C(12)–Si	1.85(1)
Os(1)–Os(3)	2.843(1)	C(13)–Si	1.87(2)
Os(2)–Os(3)	2.836(1)	C(14)–Si	1.82(2)
Os(1)–C(1)	1.95(1)	C(15)–Si	1.83(2)
Os(1)–C(2)	1.89(1)	C(11)–C(12)	1.24(2)
Os(1)–C(3)	1.90(1)	C(1)–O(1)	1.11(2)
Os(1)–C(11)	2.02(1)	C(2)–O(2)	1.13(2)
Os(2)–C(4)	1.92(1)	C(3)–O(3)	1.13(2)
Os(2)–C(5)	1.92(1)	C(4)–O(4)	1.13(1)
Os(2)–C(6)	1.88(1)	C(5)–O(5)	1.11(2)
Os(2)–C(11)	2.32(1)	C(6)–O(6)	1.13(2)
Os(2)–C(12)	2.53(1)	C(7)–O(7)	1.11(2)
Os(3)–C(7)	1.94(1)	C(8)–O(8)	1.17(1)
Os(3)–C(8)	1.91(1)	C(9)–O(9)	1.14(2)
Os(3)–C(9)	1.89(1)	C(10–O(10)	1.12(2)
Os(3)–C(10)	1.94(1)		

Os(1)–Os(3)–Os(2)	60.5(1)	C(7)–Os(3)–C(8)	91.5(5)
Os(3)–Os(1)–Os(2)	59.6(1)	C(7)–Os(3)–C(9)	101(1)
Os(1)–Os(2)–Os(3)	59.9(1)	C(8)–Os(3)–C(9)	90.6(5)
Os(1)–C(11)–C(12)	167(1)	C(7)–Os(3)–C(10)	93(1)
Os(2)–C(11)–C(12)	85(1)	C(8)–Os(3)–C(10)	172.5(5)
Os(2)–C(12)–C(11)	66(1)	C(9)–Os(3)–C(10)	94(1)
Si–C(12)–C(11)	162(1)	Os(1)–Os(2)–C(6)	112.3(4)
Si–C(12)–Os(2)	132(1)	Os(2)–Os(1)–C(1)	117.0(4)
C(13)–Si–C(12)	109(1)	Os(2)–Os(3)–C(10)	85.9(4)
C(14)–Si–C(12)	104(1)	Os(1)–Os(3)–C(10)	87.2(4)
C(14)–Si–C(13)	112(1)	Os(2)–Os(3)–C(8)	87.5(3)
C(15)–Si–C(12)	110(1)	Os(1)–Os(3)–C(8)	86.4(4)
C(15)–Si–C(13)	110(1)	Os(2)–Os(3)–C(7)	101.5(5)
C(1)–Os(1)–C(2)	92.4(5)	Os(1)–Os(2)–C(4)	113.2(4)
C(1)–Os(1)–C(3)	94.2(5)	Os(2)–Os(1)–C(3)	113.6(4)
C(2)–Os(1)–C(3)	95.4(5)	Os(1)–Os(3)–C(9)	96.6(4)
C(4)–Os(2)–C(5)	100.5(5)	Os(1)–C(11)–Os(2)	82.0(4)
C(4)–Os(2)–C(6)	92.4(5)	Os(1)–Os(2)–C(11)	44.4(3)
C(5)–Os(2)–C(6)	91(1)	Os(2)–Os(1)–C(11)	53.6(3)



(*a*) (*b*)

Fig. 4 Space-filling pictures of compounds **2** (*a*) and **3** (*b*) showing a 'hole' along the Os–Os edge in which the H(hydride) is probably located

whole ligand electronic system (with respect to that of 'free' $HCCSiMe_3$) is more perturbed than in **3**. Compound **2** is isostructural and isomorphous with the recently reported iron complex $[FeH(CO)_9(CCSiMe_3)]$.[14] On the contrary, no other examples of μ-η^2 $CCSiMe_3$ ligands are, to our knowledge, known. A comparable bonding situation has been observed in complexes containing the $C{\equiv}CPh$ group, such as $[Os_3H(CO)_9(PMe_2Ph)(C{\equiv}CPh)]$[11] and $[Os_3(CO)_{10}(C{\equiv}CPh)\{Au(PMe_2Ph)\}]$.[10] Direct location of the H(hydride) atoms was not achieved in both X-ray studies. As discussed previously the H-atom position in **2** cannot be inferred on the basis of the M–M bond-lengthening effect which usually accompanies the presence of μ-H ligands in hydrido carbonyl clusters. It was possible, however, to detect the presence of a large 'niche' in the CO ligand envelope [see Fig. 4(*a*)] along the Os(1)–Os(2) bond. This attribution is substantiated by a neutron diffraction study of the related species $[Ru_3H(CO)_9(C{\equiv}CBu^t)]$[20] where the H atom was found to span the Ru–Ru bond bearing the $C{\equiv}C$ ($\perp$) system. In **3** both Os–Os bond lengthening and the presence of a 'hole' in the ligand coverage [see Fig. 4(*b*)] concur in locating the H(hydride) atom in μ-bridging position along the Os(1)–Os(2) bond. In this context it is interesting that, in keeping with the isolobal analogy between the H and $AuPR_3$ groups,[21] the supposed H(hydride) position in **3** is the same as that of the $AuPMe_2Ph$ fragment in the structure of the above-mentioned cluster $[Os_3(CO)_{10}(CCPh)\{Au(PMe_2Ph)\}]$.[10]

Experimental

All reactions were carried out under nitrogen although subsequent work-up was carried out without exclusion of air. All the solvents were freshly distilled under nitrogen from standard drying agents. Infrared spectra were recorded on Perkin-Elmer PE 983 or 1710 F.T.I.R. spectrometers, mass spectra on Kratos A.E.I. MS 12 or MS 80 instruments, ^1H NMR spectra on a Bruker WM 250 instrument in CD_2Cl_2 or $CDCl_3$ solvents and ^{13}C NMR spectra on a Bruker AM 400 instrument in $CDCl_3$ solvent using $CDCl_3$ or CD_2Cl_2 as the internal reference. Products were separated in air by TLC on 20 × 20 cm glass plates coated with a 0.25 mm layer of Merck Kieselgel 60 F_{254} using hexane as eluent. The clusters $[Os_3(CO)_{10}(MeCN)_2]$ and $[Os_3H(CO)_{10}Cl]$ were prepared by the literature method.[18]

Synthesis of $[Os_3(CO)_{10}(HCCSiMe_3)]$ **1**.—The compound $[Os_3(CO)_{10}(MeCN)_2]$ (0.060 g, 0.064 mmol) was stirred in CH_2Cl_2 (15 cm^3) with an excess of Me_3SiC_2H. The solution immediately changed from light yellow to deep orange and the solvent was removed under vacuum after 15 min. The residue was subjected to TLC on silica plates, using hexane as eluent, yielding one orange band which was characterized as $[Os_3(CO)_{10}(HCCSiMe_3)]$ **1** (0.054 g, 88%). Repetition of the reaction with a 1:1 molar ratio of $[Os_3(CO)_{10}(MeCN)]$ to trimethylsilylacetylene and subsequent work-up as above gave again compound **1** in high yield.

Thermolysis of $[Os_3(CO)_{10}(HCCSiMe_3)]$ **1**.—Compound **1** (0.070 g, 0.074 mmol) was dissolved in heptane (20 cm^3) and refluxed for 2 h at 70 °C until a spot TLC revealed disappearance of the starting material and the solution turned pale yellow. Evaporation of the solvent followed by separation on thin silica plates eluting with hexane afforded two white products. The first band contained $[Os_3H(CO)_9(CCSiMe_3)]$ **2** (0.039 g, 58%) which was crystallized from CH_2Cl_2–hexane mixtures at −20 °C to afford colourless platelets of **2** (Found: C, 18.30; H, 1.20. Calc.: C, 18.25; H, 1.10%); $\delta_C(CDCl_3)$: 1.49 [3 C, s, $Si(CH_3)_3$], 48.71 [1 C, s, $C{\equiv}CSi(CH_3)_3$], 144.27 [1 C, s, $C{\equiv}CSi(CH_3)_3$], 162.37, 169.43 and 172.40 (all s, CO). The second fraction was $[Os_3H(CO)_9(CCH)]$ (0.015 g, 24%) identified by comparison of IR and NMR spectroscopic data with those in the literature.[7]

Reaction of $[Os_3H(CO)_9(C{\equiv}CSiMe_3)]$ **2** *with Methanol*.—The compound $[Os_3H(CO)_9(C{\equiv}CSiMe_3)]$ (0.050 g, 0.054 mmol) was dissolved in methanol (20 cm^3) and refluxed at 65 °C for 5 h until a spot TLC revealed the disappearance of the starting material. Removal of the solvent under vacuum followed by TLC eluting with hexane afforded whitish $[Os_3H(CO)_9(CCH)]$ (0.035 g, 77%).

Preparation of $[Os_3H(CO)_{10}(CCSiMe_3)]$ **3**.—A solution of trimethylsilylacetylene (0.100 cm^3, 0.71 mmol) in dry hexane (10 cm^3) was cooled to −20 °C and 1.6 mol dm^{-3} butyllithium (0.440 cm^3, 0.70 mmol) was added. The mixture was then stirred

Table 4 Crystal data and details of measurements for compounds **2** and **3**

	2	**3**
Formula	$C_{14}H_{10}O_9Os_3Si$	$C_{15}H_{10}O_{10}Os_3Si$
M	920.91	948.90
Crystal size/mm	0.11 × 0.11 × 0.20	0.10 × 0.10 × 0.13
System	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	9.201(2)	13.338(5)
b/Å	13.127(2)	9.141(4)
c/Å	9.118(7)	18.902(7)
α/°	107.31(3)	—
β/°	98.57(3)	109.99(3)
γ/°	93.18(2)	—
U/Å^3	1033.8	2165.6
Z	2	4
F(000)	816	1688
D_c/g cm^{-3}	2.96	2.91
μ(Mo-Kα)/cm^{-1}	196.5	187.7
Scan mode	ω–2θ	ω–2θ
θ range/°	2.5–25	3–25
ω-Scan width/°	0.70	0.85
Requested counting, $\sigma(I)/I$	0.01	0.02
Prescan rate/min^{-1}	6	8
Prescan acceptance, $\sigma(I)/I$	0.5	0.5
Maximum scan time/s	100	100
Octants explored	$\pm h, \pm k, +l$	$\pm h, +k, +l$
Measured reflections	3872	3452
Unique observed reflections used in refinement	2956	3004
Absorption correction (minimum, maximum)	0.85, 1.00[a]	0.53, 1.00[b]
R, R', S[c]	0.033, 0.035, 0.92	0.042, 0.043, 0.82
k, g	1.00, 0.0021	1.00, 0.0044

[a] Applied by the Walker and Stuart method.[22] [b] Applied by azimuthal scanning of reflections at $\chi > 80$.[23] [c] $R' = \Sigma[(F_o - F_c)w^{\frac{1}{2}}]/\Sigma(F_o w^{\frac{1}{2}})$, where $w = k/[\sigma^2(F) + |g|F^2]$.

Table 5 Fractional atomic coordinates for compound **2**

Atom	x	y	z
Os(1)	0.914 56(4)	0.816 07(3)	0.154 52(4)
Os(2)	0.709 24(4)	0.810 90(3)	0.355 58(4)
Os(3)	0.924 02(4)	0.661 81(3)	0.317 80(4)
Si	0.524 5(3)	0.714 2(2)	−0.069 4(3)
C(1)	0.973 3(11)	0.741 1(7)	−0.035 6(12)
O(1)	1.005 8(10)	0.698 4(7)	−0.155 8(11)
C(2)	0.870 2(10)	0.938 4(8)	0.086 1(11)
O(2)	0.845 3(9)	1.012 4(6)	0.052 5(10)
C(3)	1.113 0(11)	0.861 4(8)	0.251 8(13)
O(3)	1.233 0(9)	0.887 3(8)	0.314 7(13)
C(4)	0.544 6(12)	0.729 2(9)	0.384 8(12)
O(4)	0.445 8(10)	0.679 2(9)	0.401 8(12)
C(5)	0.600 9(12)	0.930 6(8)	0.346 2(12)
O(5)	0.544 3(10)	1.005 4(7)	0.342 9(10)
C(6)	0.788 2(12)	0.855 8(8)	0.571 7(12)
O(6)	0.841 1(11)	0.881 2(7)	0.702 1(9)
C(7)	0.851 2(12)	0.562 4(9)	0.411 5(13)
O(7)	0.805 4(10)	0.502 1(8)	0.464 4(12)
C(8)	1.055 5(11)	0.570 9(8)	0.210 7(14)
O(8)	1.135 8(9)	0.519 2(7)	0.149 3(10)
C(9)	1.072 8(12)	0.734 8(10)	0.493 0(14)
O(9)	1.162 6(11)	0.782 4(9)	0.597 2(11)
C(10)	0.766 9(9)	0.678 0(6)	0.161 7(9)
C(11)	0.681 5(9)	0.734 2(7)	0.095 3(11)
C(12)	0.368 5(15)	0.640 7(13)	−0.025 7(17)
C(13)	0.582 9(16)	0.634 2(12)	−0.249 4(15)
C(14)	0.473 9(17)	0.844 8(10)	−0.085 1(20)

for 30 min at that temperature. Subsequently 1.60 cm^3 of this solution containing Li[CCSiMe$_3$] (0.113 mmol) was added by syringe to a solution of the compound [$Os_3H(CO)_{10}Cl$] (0.100 g, 0.113 mmol) in hexane (25 cm^3) at 0 °C and the reaction monitored by IR spectroscopy. It was complete after 45 min stirring, with a change in colour from light yellow to orange. The reaction mixture was then filtered and reduced in volume. The resulting solution was separated on thin silica plates eluting with hexane to give as a first fraction a yellow solid. This was crystallized from pentane solutions at −20 °C to afford orange crystals of compound **3** (46 mg, 42%) (Found: C, 18.85; H, 1.20. $C_{15}H_{10}O_{10}Os_3Si$ requires C, 19.00; H, 1.05%).

Alternatively, to a solution of [$Os_3(CO)_{11}$(MeCN)] (50 mg, 0.05 mmol) in CH_2Cl_2 (15 cm^3) was added a two-fold excess of trimethylsilylacetylene at room temperature. The solution changed from light yellow to orange upon addition of the acetylene and the solvent was removed under vacuum after 5 min stirring. Work-up by TLC eluting with CH_2Cl_2–hexane (4:6 v/v) gave [$Os_3H(CO)_{10}$(CCSiMe$_3$)] **3** (0.031 g, 60%).

Thermolysis of [$Os_3H(CO)_{10}(C{\equiv}CSiMe_3)$] **3**.—A solution of compound **3** (0.050 g, 0.053 mmol) in heptane (30 cm^3) was heated under reflux. Analytical TLC and IR spectroscopy were used to monitor the reaction and after 6 h showed that all the starting material had been consumed. The solution was evaporated to dryness and the residue subjected to chromatography on silica plates eluting with hexane. Two white bands were separated: [$Os_3H(CO)_9(C{\equiv}CSiMe_3)$] (0.0315 g, 65%) as the first fraction and [$Os_3H(CO)_9(C{\equiv}CH)$] (8 mg, 18%) as the second.

X-Ray Structure Determinations.—Crystal data and details of the measurements for compounds **2** and **3** are reported in Table 4. Diffraction intensities were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer equipped with Mo-Kα radiation (λ = 0.710 69 Å), corrected for Lorentz-polarization effects and reduced to F_o. No correction for decay was necessary. An empirical absorption correction was applied for compound **3** using the azimuthal scan method.[23] The metal-atom positions were determined by direct methods and all remaining atoms located from subsequent Fourier difference syntheses. An absorption correction was applied for compound **2** by the Walker and Stuart method[22] once the structural model

Table 6 Fractional atomic coordinates for compound **3**

Atom	*x*	*y*	*z*
Os(1)	0.342 23(4)	0.373 29(5)	0.119 54(2)
Os(2)	0.168 55(3)	0.193 88(5)	0.031 70(2)
Os(3)	0.380 73(3)	0.087 11(5)	0.075 72(2)
Si	0.117 4(3)	0.431 6(4)	−0.156 2(2)
C(1)	0.412 3(10)	0.318 3(14)	0.225 0(7)
O(1)	0.451 5(9)	0.282 9(12)	0.284 2(5)
C(2)	0.471 7(9)	0.439 0(15)	0.110 3(7)
O(2)	0.546 9(8)	0.471 3(13)	0.099 2(6)
C(3)	0.299 0(10)	0.560 4(14)	0.142 6(7)
O(3)	0.274 6(11)	0.671 8(13)	0.156 6(8)
C(4)	0.031 4(9)	0.283 2(15)	0.013 0(7)
O(4)	−0.051 5(8)	0.327 9(14)	0.002 6(7)
C(5)	0.137 6(11)	0.068 2(13)	−0.054 3(8)
O(5)	0.119 4(9)	−0.006 1(12)	−0.103 4(6)
C(6)	0.138 3(9)	0.042 2(16)	0.088 8(8)
O(6)	0.117 9(8)	−0.049 3(12)	0.121 7(6)
C(7)	0.358 2(12)	−0.109 6(14)	0.034 0(7)
O(7)	0.347 7(11)	−0.222 4(12)	0.010 9(7)
C(8)	0.363 6(9)	0.021 5(13)	0.166 8(7)
O(8)	0.353 2(8)	−0.018 5(11)	0.222 5(5)
C(9)	0.530 7(10)	0.090 3(14)	0.123 2(8)
O(9)	0.621 3(8)	0.099 2(15)	0.150 8(6)
C(10)	0.385 0(11)	0.174 1(15)	−0.017 0(9)
O(10)	0.390 7(9)	0.217 1(12)	−0.071 3(6)
C(11)	0.257 1(9)	0.397 8(12)	0.008 9(6)
C(12)	0.192 1(10)	0.389 7(14)	−0.056 1(6)
C(13)	0.154 8(16)	0.295 0(20)	−0.216 4(8)
C(14)	0.158 8(17)	0.615 8(21)	−0.169 6(11)
C(15)	−0.025 8(13)	0.423 8(20)	−0.173 4(9)

was completely defined and all atoms refined isotropically. For all computations the SHELX 76 package of crystallographic programs was used.[24] In both compounds **2** and **3** all atoms, except the H atoms, were allowed to vibrate anisotropically. Hydrogen atoms were added in calculated positions (C–H 1.08 Å) and refined 'riding' on their corresponding C atoms. A common isotropic thermal parameter was refined for the H atoms (0.14 $Å^2$ for **2** and 0.10 $Å^2$ for **3**, respectively). Attempts to locate the H(hydride) atom position from Fourier difference maps for **2** and **3** gave untrustworthy results and were abandoned. A final difference map showed no significant regions of electron density except for residual peaks of *ca.* 2.0 e $Å^{-3}$ close to the Os atom positions in **2** and in **3**. The final atomic coordinates are presented in Tables 5 and 6, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

We thank the EEC and the Ministero della Universita' e della Ricerca Scientifica e Tecnologica (M.U.R.S.T.) for financial support.

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Received 18*th July* 1991; *Paper* 1/03664E