

# Reaction of $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ with the diyne $\text{Me}_3\text{SiC}_2\text{C}_2\text{SiMe}_3$ and the reactivity of the products towards $[\text{Co}_2(\text{CO})_8]$ : the X-ray structures of $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\{\mu\text{-}\eta^1\text{-}\eta^2\text{-HC}_2(\text{SiMe}_3)\text{C}_2(\text{SiMe}_3)\}]$ , $[\text{Os}_3(\mu\text{-CO})(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}_2\text{SiMe}_3\}]$ and $[\text{Os}_3(\mu\text{-H})(\text{CO})_9\{\mu_3\text{-}\eta^1\text{:}\eta^2\text{-};\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}_2[\text{Co}_2(\text{CO})_6]\}]$

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## Abstract

The reaction of  $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$  with  $\text{Me}_3\text{SiC}_2\text{C}_2\text{SiMe}_3$  affords both  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\{\mu\text{-}\eta^1\text{-}\eta^2\text{-HC}_2(\text{SiMe}_3)\text{C}_2(\text{SiMe}_3)\}]$  (**1**) and  $[\text{Os}_3(\mu\text{-CO})(\text{CO})_9(\mu_3\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}_2\text{SiMe}_3)]$  (**2**) in good yield, **2** being favoured with an excess of diyne. In **1**, one edge of the triosmium unit is bridged by the vinyl moiety of a transformed bis(trimethylsilyl)-1,4-butadiyne ligand that has undergone a hydride transfer and a 1,2-trimethylsilyl shift. Compound **2** is selectively desilylated in methanol to produce a single isomer of the known cluster  $[\text{Os}_3(\mu\text{-CO})(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-HC}_2\text{C}_2\text{SiMe}_3\}]$  (**3**). Whereas reaction of **3** with  $[\text{Co}_2(\text{CO})_8]$  results in the production of the previously reported cluster  $[\text{Os}_3\{\mu_3\text{-}\eta^2\text{-};\mu\text{-}\eta^2\text{-}(\text{Me}_3\text{SiC}_2\text{C}_2\text{H})[\text{Co}_2(\text{CO})_6\}\}(\mu\text{-CO})(\text{CO})_9]$  (**4**) and a second product  $[\text{Os}_3(\mu\text{-H})(\text{CO})_9\{\mu_3\text{-}\eta^1\text{:}\eta^2\text{-};\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}_2[\text{Co}_2(\text{CO})_6]\}]$  (**5**), the reaction of **1** and **2** results in recovery of the starting material or transfer of the alkyne ligand to the  $\text{Co}_2$  unit. Compound **4** undergoes a transformation to **5** in visible light. All the cluster complexes have been characterized spectroscopically, and the solid-state structures of **1**, **2** and **5** have been determined by single-crystal X-ray diffraction. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Osmium; Cobalt; Carbonyl cluster; Diyne; X-ray crystal structure

## 1. Introduction

The interaction between di-yne and poly-yne and mono- and polynuclear organometallic species is attracting considerable attention at present. This is because of the novel reactivity of these species that allows metal fragments to be linked together to form oligomeric and polymeric species, and because of the novel electronic properties that these materials exhibit [1]. The reactions of diyne ligands with hydrido-substituted ruthenium and osmium clusters are of particular interest from the viewpoint of their reactivity because of the key role that the metal hydrides play in their

formation and subsequent chemistry. In this context Carty and co-workers have described the reaction of the phosphinidene cluster  $[(\mu\text{-H})_2\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-PPH})]$  with  $\text{PhC}_2\text{C}_2\text{Ph}$  and we have recently investigated the reactions of the diynes  $\text{RC}_2\text{C}_2\text{R}$  ( $\text{R} = \text{Me}, \text{Ph}, \text{SiMe}_3$ ) with  $[(\mu_2\text{-H})_4\text{Ru}_4(\text{CO})_{12}]$  [2]. All these reactions are characterized by 1,1-, 1,2- or 1,4-dihydrogenations of the diyne ligand to form dienediyl or enyne ligands.

It is well established that  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}]$  catalyses the hydrogenation and isomerisation of 1-alkenes to internal alkenes at room temperature, via alkenyl intermediates [3]. In the presence of excess alkyne  $\text{R}'\text{CCR}'$ , alkenes,  $\text{RHCCHR}'$  may be liberated from hydrido alkenyl complexes of the type  $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^1\text{-}\eta^2\text{-RC=CHR}')]$ , with the formation of  $[\text{Os}_3(\text{CO})_{10}(\mu_3\text{-}\eta^2\text{-R}'\text{CCR}')]$  clusters or metallacyclic complexes, e.g.

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$[\text{Os}_3(\text{CO})_9(\mu_2\text{-}\eta^4\text{-R'CC(R)C(R)CR'})]$  and  $[\text{Os}_3(\text{CO})_9(\mu_3\text{-}\eta^4\text{-R'CC(R)C(=O)C(R)CR'})]$  [4]. The alkene may be produced with either a *trans*- or *cis*-configuration [5].

In contrast, Carty has shown that the reaction of the dinuclear iron complex  $[(\mu\text{-H})\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)]$  with diynes yields alkenyl complexes  $[\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)(\mu_2\text{-}\eta^1\text{-}\eta^2\text{-C(CCR)=CHR})]$  ( $\text{R} = \text{Me}, \text{Ph}$ ), in these examples the -yne function is not coordinated [6]. Whereas the initial product of the reaction of  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}]$  with the functionalised diyne  $\text{HOCH}_2\text{C}_2\text{C}_2\text{CH}_2\text{OH}$  is thought to involve alkenyl coordination, however, it subsequently undergoes a novel cyclisation and dehydration to afford  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}(\mu_2\text{-}\eta^3\text{-O-CH=CH-C=C-CH}_3)]$ , that contains a furan ring [7]. Similar cyclisations have been observed in the reaction of  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}]$  with  $\text{PhC}_2\text{C}_2\text{Ph}$  [8].

In complexes with free alkyne groups, the cluster may be reactive towards other organometallic fragments. The reactions of  $[\text{M}_3(\text{CO})_9(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{-RC}_2\text{C}_2\text{R}')] ]$  with  $[\text{Co}_2(\text{CO})_8]$  demonstrate a difference in reactivity between the Ru and Os analogues; for  $\text{M} = \text{Ru}$ ,  $\text{R} = \text{R}' = \text{Ph}$  Ru–Ru and Co–Co bond cleavage occurs to generate  $[\text{Co}_2\text{Ru}_3(\mu_5\text{-}\eta^2, \eta^2\text{-PhC}_2\text{C}_2\text{Ph})]$  with a bow-tie metal core, whereas for  $\text{M} = \text{Os}$ ,  $\text{R} = \text{H}$ ,  $\text{R}' = \text{SiMe}_3$  or  $\text{R} = \text{R}' = \text{Me}$  a  $[\text{Co}_2(\text{CO})_6]$  unit coordinates to the free  $\text{C}\equiv\text{C}$  bond in a  $\mu\text{-}\eta^2$  manner [9,10]. In this paper, we compare the reactions of  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}]$  with the diyne  $\text{Me}_3\text{SiC}_2\text{C}_2\text{SiMe}_3$ , and investigate the reactions of the products with  $[\text{Co}_2(\text{CO})_8]$ .

## 2. Results and discussion

When a purple solution of  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}]$  is stirred with one molar equivalent of 1,4-bis(trimethylsilyl)butadiyne at room temperature, the solution turns brown over a period of 24 h. The work-up of the product on silica plates results in the isolation of both a brown and an orange–brown product. Analysis of the  $^1\text{H-NMR}$  and IR spectra suggests the formulation  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-}\eta^1\text{-}\eta^2\text{-HC}_2(\text{SiMe}_3)\text{C}_2(\text{SiMe}_3))]$  (**1**) for the brown product. The mass spectrum indicates an intense molecular ion peak at  $m/z = 1046$ , confirming that a reaction of the ligand with the hydrido-cluster has occurred. A  $\mu\text{-}\eta^2$  alkenyl coordination mode may be established on the basis of a resonance at  $\delta 7.98$  ppm in the  $^1\text{H-NMR}$  spectrum, resolved as a doublet due to coupling to the bridging hydride ( $^3J = 1.8$  Hz). This was confirmed by a  $^1\text{H-NMR}$  decoupling experiment, which shows a collapse of the mutual coupling exhibited by both resonances. The  $^3J$  proximity required to produce a coupling via the osmium vertex suggests that a 1,2-trimethylsilyl shift ligand must have occurred so that the H atom is attached to the  $\sigma$ -bound C atom. Two discrete trimethylsilyl signals are observed in both the  $^1\text{H}$ - and  $^{13}\text{C-NMR}$  spectra and the IR spectrum shows a characteristic  $\nu(\text{C}\equiv\text{C})$  free triple bond absorption at  $2132\text{ cm}^{-1}$ .

The molecular structure of **1** has been confirmed by a single-crystal X-ray analysis. The molecular structure is shown in Fig. 1 while selected bond parameters are

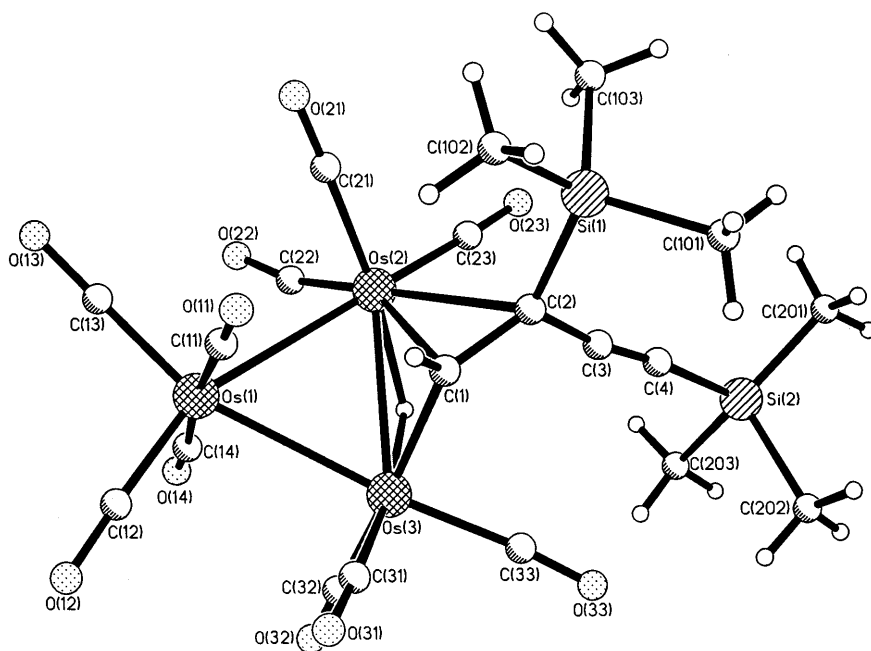


Fig. 1. The molecular structure of  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}\{\mu\text{-}\eta^1\text{-}\eta^2\text{-HC}_2(\text{SiMe}_3)\text{C}_2(\text{SiMe}_3)\}]$  (**1**) showing the atom numbering scheme adopted.

Table 1  
Selected bond lengths (Å) and angles (°) for **1**

Os(1)–Os(2)	2.9044(2)	C(2)–Si(1)	1.89(2)
Os(2)–Os(3)	2.8506(14)	C(4)–Si(2)	1.84(2)
Os(1)–Os(3)	2.8648(13)	Os(2)–C(2)	2.51(3)
Os(3)–C(1)	2.10(2)	C(2)–C(3)	1.45(3)
Os(2)–C(1)	2.30(3)	C(3)–C(4)	1.18(2)
Os(1)–Os(2)–Os(3)	59.70(3)	Os(3)–C(1)–C(2)	125.4(13)
Os(1)–Os(3)–Os(2)	61.08(3)	C(2)–C(3)–C(4)	171(2)
Os(2)–Os(1)–Os(3)	59.22(3)	C(3)–C(4)–Si(2)	175(2)
Os(2)–Os(3)–C(1)	52.7(8)		

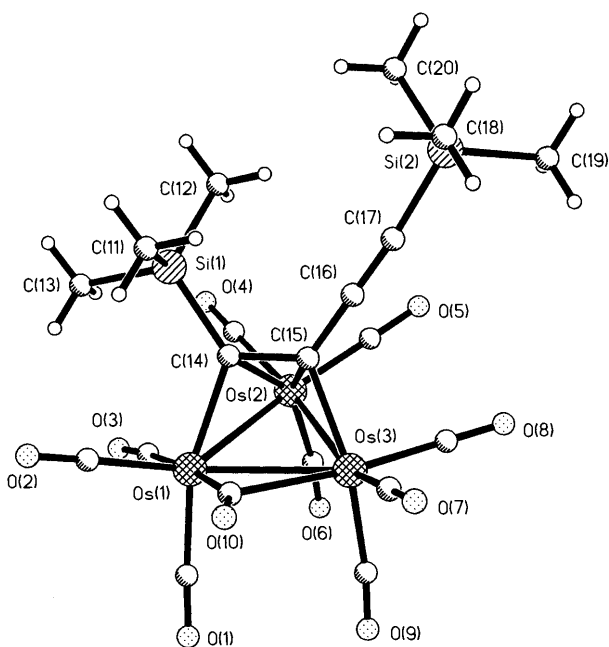


Fig. 2. The molecular structure of  $[\text{Os}_3(\mu\text{-CO})(\text{CO})_9(\mu_3\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}_2\text{SiMe}_3)]$  (**2**) showing the atom numbering scheme adopted.

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

Os(1)–Os(2)	2.7918(10)	C(14)–Si(1)	1.895(13)
Os(2)–Os(3)	2.7476(8)	C(14)–C(15)	1.43(2)
Os(1)–Os(3)	2.8637(8)	C(15)–C(16)	1.41(2)
Os(2)–C(15)	2.259(13)	C(16)–C(17)	1.23(2)
Os(2)–C(14)	2.21(2)	C(17)–Si(2)	1.82(2)
Os(1)–C(14)	2.150(12)	C(10)–O(10)	1.15(2)
Os(3)–C(15)	2.115(13)		
Os(1)–Os(2)–Os(3)	62.25(2)	C(15)–C(16)–C(17)	180(2)
Os(2)–Os(1)–Os(3)	58.12(2)	C(16)–C(17)–Si(2)	174(2)
Os(1)–Os(3)–Os(2)	59.63(2)	Os(1)–C(10)–Os(3)	78.3(6)
Si(1)–C(14)–C(15)	122.4(10)	Os(1)–C(10)–O(10)	154(2)
C(14)–C(15)–C(16)	125.4(12)	Os(3)–C(10)–O(10)	126.8(13)

listed in Table 1. The ligand donates three electrons in this  $\mu\text{-}\eta^2$  alkenyl coordination mode, one through the  $\sigma$ -interaction and two via the  $\pi$ -bond of the bridging metallated olefin, such that the electron count for the cluster is the  $48 e^-$  expected for a triangular metal core.

The atom C(1) is bound to Os(3) via a  $\sigma$ -bond while C(1) and C(2) exhibit a  $\pi$ -interaction to Os(2). Several differently substituted alkyne analogues of this have been reported previously [11] but none in which a 1,2-trimethylsilyl shift has occurred. However, similar 1,2-trimethylsilyl shifts have been observed in some dinuclear ruthenium systems [12]. The Si(1)Me<sub>3</sub> group that was coordinated to C(1) in the free ligand has undergone a 1,2-shift to C(2) while a hydride has been transferred from the triosmium core to the C(1) atom. The ligand is bent away from the metal core because of the formal rehybridization of the alkylenic carbon atoms upon coordination to the metal framework, as is observed in all alkenyl complexes [11]. In this case, however, there may also be a steric component because of the steric bulk of the trimethylsilyl groups, and as a consequence the Os(2)–C(2) distance is 2.51(3) Å, considerably longer than that expected or those observed for similar alkenyl complexes, typically falling in the range 2.30–2.40 Å [11]. The free alkyne moiety, C(3)–C(4) is almost linear with C(2)–C(3)–C(4) and C(3)–C(4)–Si(2) angles of 171(2) and 175(2)°, respectively and exhibits a typical alkyne bond length of 1.18(2) Å. The C(1)–C(2) length is 1.42(2) Å, characteristic of this type of alkenyl coordination. The hydride was not located directly but potential energy calculations [13] indicate that it bridges the Os(2)–Os(3) edge. The ten carbonyl ligands are all terminally bound and essentially linear. The <sup>13</sup>C-NMR spectrum exhibits ten resonances in the carbonyl region indicating that the CO ligands are static on the NMR time scale at room temperature.

The orange product of the reaction has been identified spectroscopically as the previously reported cluster,  $[\text{Os}_3(\mu\text{-CO})(\text{CO})_9(\mu_3\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}_2\text{SiMe}_3)]$  (**2**) [14]. This product is formed in greater yield when an excess of bis(trimethylsilyl)butadiyne is added to the reaction mixture and is also generated when a CH<sub>2</sub>Cl<sub>2</sub> solution of **1** is treated with the free ligand. This behaviour is well-established for Os<sub>3</sub> alkenyl clusters as discussed in the introduction; however, it is interesting to note that intramolecular substitution by the free -yne unit does not occur, which may be due in part to the greater steric demand of the transformed  $\{(\mu\text{-}\eta^1\text{-}\eta^2\text{-HC}_2(\text{SiMe}_3)_2\text{C}_2(\text{SiMe}_3))\}$  ligand.

Since a structural analysis of **2** has not been reported, a single crystal, grown from a pentane solution of **2**, has been analysed by single-crystal X-ray crystallography. The molecular structure of **2** is presented in Fig. 2 and selected bond parameters are given in Table 2. The molecular structure consists of a closed triosmium unit, capped by a 1,4-bis(trimethylsilyl)butadiyne ligand in a classical  $\mu_3\text{-}\eta^2$  manner, creating a nido-octahedral M<sub>3</sub>C<sub>2</sub> core geometry. A trimethylsilylethynyl moiety remains uncoordinated to the triosmium core and is essentially linear and free alkyne bond length

C(16)–C(17) of 1.23(2) Å is in the expected range. The triosmium unit is coordinated by nine terminally bound CO ligands, and a single asymmetrically bridging carbonyl ligand on the Os(1)–Os(3) edge. The Os-bound alkyne bond length, C(14)–C(15) shows a characteristic lengthening to 1.43(2) Å, as expected for a  $\mu_3$ - $\eta^2$  bound alkyne unit.

Cluster **2** undergoes facile desilylation upon standing in methanol, resulting in the formation of a single isomer of  $[\text{Os}_3(\mu_3\text{-}\eta^2\text{-HC}_2\text{C}_2\text{SiMe}_3)(\mu\text{-CO})(\text{CO})_9]$  (**3**). This complex has been reported recently, being obtained from the reaction of  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$  with  $\text{HC}_2\text{C}_2\text{SiMe}_3$ , where both possible isomers were observed, in a 2:1 ratio [9,10].

### 2.1. Reaction of $[\text{Co}_2(\text{CO})_8]$ with **1**, **2** and **3**

The products **1**, **2** and **3** have been treated with  $[\text{Co}_2(\text{CO})_8]$  to investigate the steric accessibility of the free alkyne moieties. In the reaction of **1**, the only Os-containing product that could be isolated has been identified spectroscopically as the starting material. The free triple bond in **1** is sterically crowded, C(3) and C(4) being shielded between Si(1) and Si(2), leading to the low reactivity towards small organometallic fragments such as  $[\text{Co}_2(\text{CO})_8]$ . Similarly, **2** shows no propensity to add a dicobalt unit. Again, the sterically demanding trimethylsilyl groups are in close proximity and the free

triple bond is inaccessible, in contrast to the free alkyne in  $[\text{Os}_3(\text{CO})_{10}(\mu_3\text{-}\eta^2\text{-MeCCC}_2\text{Me})]$  which does add ' $\text{Co}_2(\text{CO})_6$ '.

In contrast, ' $\text{Co}_2(\text{CO})_6$ ' addition is achieved with **3**, as has been reported previously [9]. A dichloromethane solution of **3** was stirred at room temperature with a slight molar excess of  $[\text{Co}_2(\text{CO})_8]$ . This resulted in the isolation of two dark green bands. The major dark green band (lower  $R_f$ ) afforded dark green crystals that were spectroscopically identified as the recently reported cluster  $[\text{Os}_3\{\mu_3\text{-}\eta^2\text{-}\mu\text{-}\eta^2\text{-}(\text{Me}_3\text{SiC}_2\text{C}_2\text{H})[\text{Co}_2(\text{CO})_6]\}(\mu\text{-CO})(\text{CO})_9]$  (**4**), in which the triosmium unit is capped by a  $\text{HC}_2\text{C}_2\text{SiMe}_3$  ligand in a  $\mu_3$ -( $\eta^2$ -||) fashion [9]. The second product was isolated in 35% yield and identified by spectroscopic methods. A high-field proton resonance is observed at  $\delta$  –18.70 ppm, suggests the presence of an edge-bridging hydride ligand, and the  $\text{SiMe}_3$  resonance is evident at  $\delta$  0.26 ppm. An intense  $[\text{M} - \text{CO}]^+$  peak is seen in the mass spectrum at  $m/z = 1204$ , with subsequent loss of  $n$  CO ( $n = 1\text{--}5$ ). Dark green crystals were subsequently grown from a  $\text{CH}_2\text{Cl}_2$  solution, and the molecular structure confirmed by a single crystal X-ray analysis as the new cluster mixed-metal diyne-linked cluster  $[\text{Os}_3(\mu\text{-H})(\text{CO})_9\{\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}_2\text{H}[\text{Co}_2(\text{CO})_6]\}]$  (**5**). The molecular structure is shown in Fig. 3 and selected bond lengths and angles are listed in Table 3. The diyne ligand in **5** is coordinated to the Os triangle in a

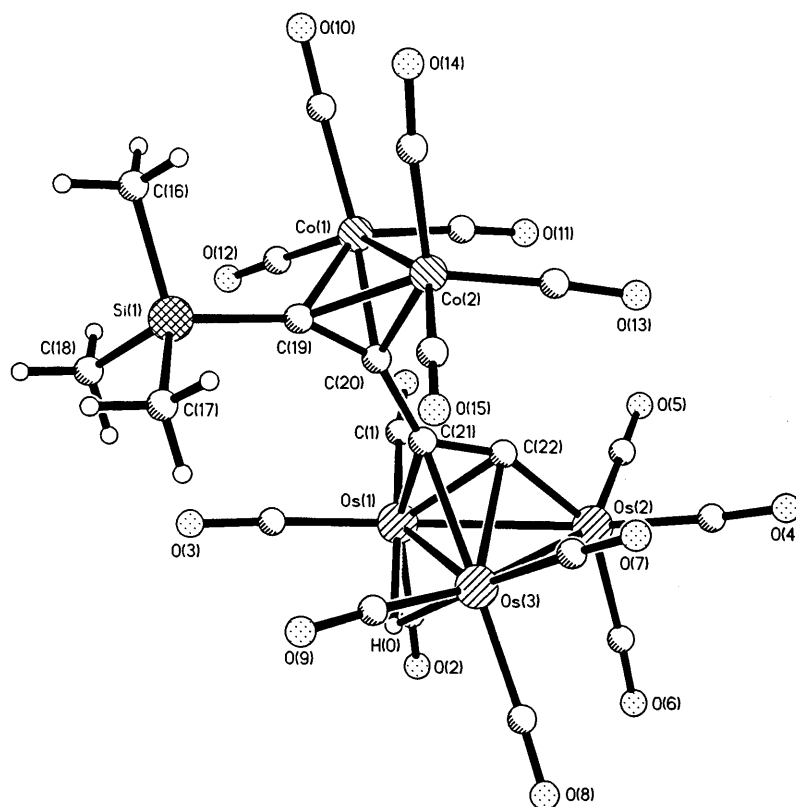


Fig. 3. The molecular structure of  $[\text{Os}_3(\mu\text{-H})(\text{CO})_9\{\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}_2\text{H}[\text{Co}_2(\text{CO})_6]\}]$  (**5**) showing the atom numbering scheme adopted.

Table 3  
Selected bond lengths (Å) and angles (°) for **5**

Os(1)–Os(2)	2.877(2)	C(20)–C(21)	1.46(2)
Os(2)–Os(3)	2.877(2)	C(19)–C(20)	1.35(2)
Os(1)–Os(3)	2.8343(12)	Co(1)–Co(2)	2.513(3)
Os(2)–C(22)	1.954(14)	Co(1)–C(19)	2.02(2)
Os(3)–C(21)	2.233(14)	Co(1)–C(20)	1.948(12)
Os(1)–C(21)	2.248(13)	Co(2)–C(19)	2.01(2)
Os(3)–C(22)	2.238(12)	Co(2)–C(20)	1.961(13)
Os(1)–C(22)	2.225(12)	Si(1)–C(19)	1.84(2)
C(21)–C(22)	1.31(2)		
Os(1)–Os(2)–Os(3)	59.02(4)	C(21)–C(20)–C(19)	149.7(14)
Os(2)–Os(1)–Os(3)	60.50(2)	C(20)–C(19)–Si(1)	154.9(13)
Os(1)–Os(3)–Os(2)	60.48(4)	Os(1)–C(21)–Os(3)	78.5(4)
Os(2)–C(22)–C(21)	153.8(10)	Co(2)–C(20)–Co(1)	80.0(5)
C(22)–C(21)–C(20)	133.8(12)	Co(2)–C(19)–Co(1)	77.3(6)

perpendicular  $\sigma, \pi, \pi$  manner, donating five  $e^-$  to the cluster. The carbon backbone of the coordinated diyne ligand, C(19)–C(20)–C(21)–C(22), and the silicon atom lie on an approximate non-crystallographic mirror plane which is approximately perpendicular to the Os(1)–Os(3) and Co(1)–Co(2) vectors. The C(22)–Os(2)  $\sigma$ -bond is considerably shorter than  $\pi$ -interactions observed between C(22), C(21), and the Os(1) and Os(3) atoms. As observed with compound **4**, the approach of the dicobalt unit towards the pendant  $\text{Me}_3\text{SiC}_2^-$  group is from above the plane of the osmium triangle. This is almost certainly a steric effect, the  $\text{Co}_2(\text{CO})_6$  unit adopting a position as far away from the triosmium unit as possible. The hydride was not directly located but potential energy calculations [13] indicate that it bridges the Os(1)–Os(3) edge and is located on the opposite side of the  $\text{Os}_3$  plane to the hydrocarbon group.

The molecular structure of **5** is broadly similar to that of the related cluster  $[\text{Ru}_3(\mu\text{-H})\{\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\mu\text{-}\eta^2\text{-C}_2\text{C}_2\text{SiMe}_3[\text{Co}_2(\mu\text{-dppm})(\text{CO})_4]\}(\text{CO})_9]$ , produced in the reaction of  $[\text{Co}_2(\mu\text{-}\eta^2\text{-RC}_2\text{C}_2\text{H})(\mu\text{-dppm})(\text{CO})_4]$  with  $[\text{Ru}_3(\text{CO})_{12}]$  under reflux in THF [9]. The angles in the  $\text{C}_4$  chain are comparable in both complexes, the main difference being that the C(22)–C(21)–C(20) angle is smaller [133.8(12)°] in **5** than in the Ru complex [148(2), 147(2)°]; the larger value in the latter is probably due to the presence of the dppm ligand, which is *trans* to the  $\text{SiMe}_3$  group. The C–C bond lengths in both clusters are comparable within the nominal e.s.d.s, the C(20)–C(21) distance being a typical single bond length and triple bond bound to the  $\text{Co}_2$  unit [C(19)–C(20), 1.35(2) Å] being somewhat shorter to that bound to the Os or Ru triangle [C(21)–C(22) 1.31(2) Å]; although this difference is not statistically significant, it is apparent in both complexes (Scheme 1).

Loss of the dicobalt unit from **4** and **5** is observed upon long standing in the presence of oxygen or on

addition of an oxidising agent (Fe[III] or Ce[IV]). The formation of **5** is a consequence of the activation of **4**. It is well established that ruthenium and osmium clusters coordinated by a  $\mu_3\text{-}(\eta^2\text{-})$  alkyne with a terminal proton may rearrange upon exposure to UV radiation or on heating to generate acetylides [4,15]. For **4**, this process occurs at low light levels. This may be as a consequence of the preference of the bulky  $\text{Me}_3\text{SiC}_2\text{-}\{\text{Co}_2(\text{CO})_6\}$  group to be as far from the triosmium unit as possible, a requirement that is fulfilled in the  $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2$  coordination mode. Consequently, if **4** is stirred in the presence of a broad-band UV source for 2 h, **5** is generated in almost quantitative yield. Compound **4** can be generated exclusively from **3** and  $[\text{Co}_2(\text{CO})_8]$  if the reaction vessel is blacked out and work up of the reaction takes place in the absence of visible light. In contrast, it is reported that **3** does not show the same tendency to transform to the hydridoalkynyl complex [9].

### 3. Experimental

All reactions were performed using standard Schlenk techniques under dry,  $\text{O}_2$ -free  $\text{N}_2$ . Technical grade solvents were purified by standard procedures.  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}]$  was prepared by the literature procedure [16] and hexa-1,3-diyne, 1,4-di(trimethylsilyl)butadiyne and  $[\text{Co}_2(\text{CO})_8]$  were used as supplied. IR spectra were recorded as  $\text{CH}_2\text{Cl}_2$  solutions in NaCl cell (0.5 mm path length) on a Perkin–Elmer 1710 FT spectrometer. FAB mass spectra were recorded on an AE1/Kratos MS 50 spectrometer and NMR spectra were recorded on a Bruker WH 400 FT spectrometer. The chemical shifts were referenced to residual protons in  $\text{CDCl}_3$  (7.25 ppm) or  $\text{CD}_2\text{Cl}_2$  (5.33) for  $^1\text{H}$  and to  $\text{CDCl}_3$  (77.0 ppm) for  $^{13}\text{C}$ .

#### 3.1. Reaction of $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}]$ with 1,4-bis(trimethylsilyl)butadiyne

A  $\text{CH}_2\text{Cl}_2$  solution (50  $\text{cm}^3$ ) of  $[(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}]$  (0.100 g, 0.117 mmol) was treated with one molar equivalent of 1,4-bis(trimethylsilyl)butadiyne (23 mg, 0.117 mmol), added as a  $\text{CH}_2\text{Cl}_2$  solution (5  $\text{cm}^3$ ) over the period of 30 min. After 24 h stirring at 20°C, the solvent was removed from the crude solution under reduced pressure and the resultant brown crude product was chromatographed on thin plates using hexane as eluant. A brown band (high  $R_f$ ) was recovered from the top of the plate, affording a brown oil upon solvent removal under reduced pressure. Black crystals were grown from a pentane solution at  $-20^\circ\text{C}$ . The subsequent X-ray crystallographic study identified this product as  $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-}\eta^1\text{-}\eta^2\text{-HC}_2(\text{SiMe}_3)\text{-}$

$C_2(SiMe_3)$  (**1**), recovered in 70% yield (0.085 g). Anal. Found: C, 21.37; H, 1.53. Calc. for  $C_{20}H_{20}O_{10}Os_3Si_2$ : C, 22.40; H, 1.90%. IR ( $CH_2Cl_2$ ):  $\nu(CO)$  2132w, 2079 (sh), 2059vs, 2022vs (br), 2000s, 1973s, 1956 (sh)  $cm^{-1}$ .  $^1H$ -NMR ( $CD_2Cl_2$ ):  $\delta$  7.98 (d, 1HC=C,  $^3J = 1.80$ ), 0.26 (s, 9H, Me), 0.16 (s, 9H, Me),  $-17.46$  (d, 10s-H-Os,  $^3J = 1.80$ ).  $^{13}C$ -NMR ( $CD_2Cl_2$ ):  $\delta$  207.12–171.32 (10 CO), 115.97 (s, C(H)=C), 110.24 (s, C=C), 108.99, 105.07 (2s, 2C≡C),  $-0.51$  (s, 3CH<sub>3</sub>),  $-1.61$  (s, 3CH<sub>3</sub>). MS ( $m/z$ ): 1046,  $[M]^+$ . A second, orange–brown band is isolated just below **1** and spectroscopic methods showed this to be the previously reported cluster  $[Os_3(\mu-CO)(CO)_9(\mu_3-\eta^2-Me_3SiC_2C_2SiMe_3)]$  (**2**) (15%, 18 mg). When a  $CH_2Cl_2$  solution (25  $cm^3$ ) of (**1**) (20 mg, 0.019 mmol) is treated with an excess of 1,4-bis(trimethylsilyl)butadiyne (5 mg,  $1.2 \times$  excess) (**2**) is recovered in quantitative yield.

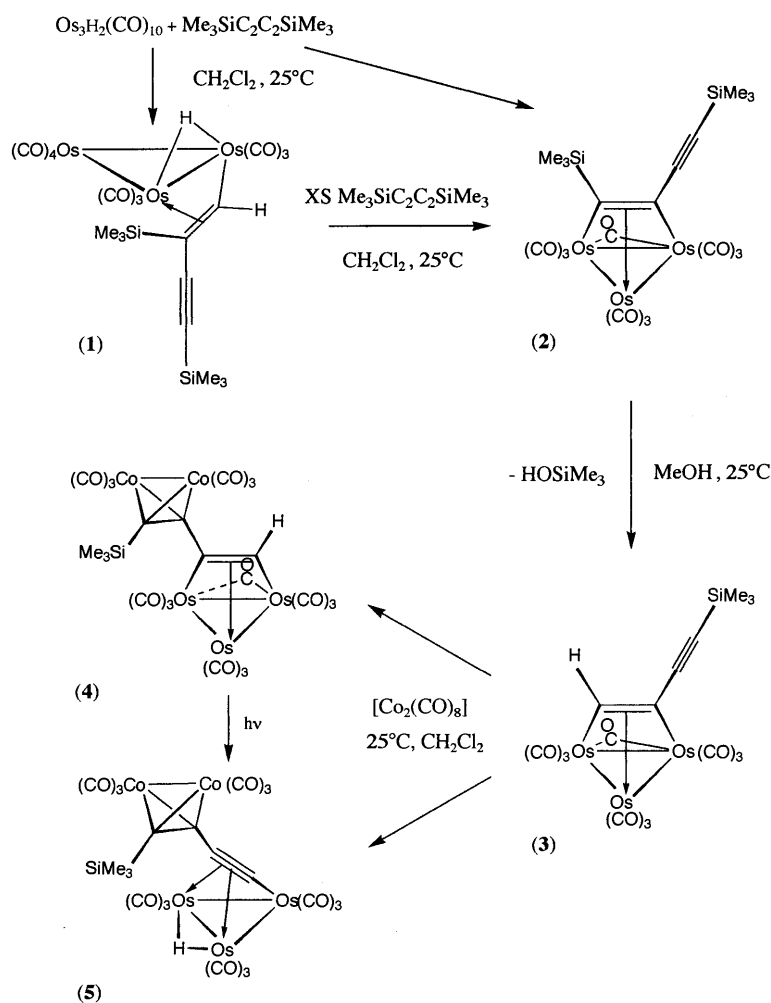
### 3.2. Reaction of **3** with $[Co_2(CO)_8]$

A  $CH_2Cl_2$  (20  $cm^3$ ) solution of (**3**) (30 mg, 0.0308 mmol) was treated with a  $CH_2Cl_2$  (10  $cm^3$ ) of

$[Co_2(CO)_8]$  (10.5 mg, 0.0308 mmol) at 20°C. Removal of solvent followed by TLC on thin plates, using hexane– $CH_2Cl_2$  (9:1) as eluent, resulted in the isolation of  $[Os_3(\mu-H)(CO)_9\{\mu_3-\eta^1:\eta^2-\mu-\eta^2-Me_3SiC_2C_2[Co_2(CO)_6]\}]$  (**5**) (35%, 13 mg) (high  $R_f$ ) from the top of the plates. Anal. Found: C, 21.50; H, 0.67. Calc. for  $C_{22}H_{10}Co_2O_{15}Os_3Si_2$ : C, 21.42; H, 0.67%. IR ( $CH_2Cl_2$ ):  $\nu(CO)$  2093s, 2081vs, 2065ms, 2036vs, 2000 (sh), 1985 (sh).  $^1H$ -NMR ( $CD_3Cl$ ):  $\delta$  0.26 (s, 9H, Me),  $-18.70$  (s, OsHOs).  $^{13}C$ -NMR ( $CD_3Cl$ ):  $\delta$  199.7 (s, 6CO), 192.46 (s, 9CO), 0.26 (s, 3CH<sub>3</sub>). MS ( $m/z$ ): 1204,  $[M - CO]^+$ . Just below **5**, a second band was recovered and identified spectroscopically as the recently reported cluster  $[Os_3\{\mu_3-\eta^2-\mu-\eta^2-(Me_3SiC_2C_2H)[Co_2(CO)_6]\}(\mu-CO)(CO)_9]$  (**4**) (60%).

### 3.3. Crystal structure determinations of **1**, **2** and **5**

Data were collected for **2** by the  $\omega/\theta$  scan method on a Stoe four-circle diffractometer and for **1** and **5** by the  $\omega/2\theta$  method on Rigaku AFC7R and AFC5R four-circle diffractometers, respectively. Three standard reflec-



Scheme 1.

Table 4  
Crystal data and refinement details for complexes **1**, **2** and **5**<sup>1</sup>

Complex	<b>1</b>	<b>2</b>	<b>5</b>
Molecular formula	C <sub>20</sub> H <sub>20</sub> O <sub>10</sub> Os <sub>3</sub> Si <sub>2</sub>	C <sub>20</sub> H <sub>18</sub> O <sub>10</sub> Os <sub>3</sub> Si <sub>2</sub>	C <sub>22</sub> H <sub>10</sub> Co <sub>2</sub> O <sub>15</sub> Os <sub>3</sub> Si
<i>M<sub>w</sub></i>	1047.14	1045.12	1230.85
Crystal system	Triclinic	Monoclinic	Triclinic
<i>a</i> (Å)	12.181(3)	9.5720(10)	12.725(6)
<i>b</i> (Å)	16.199	21.270(3)	13.775(4)
<i>c</i> (Å)	7.9140(10)	14.349(4)	9.707(3)
<i>α</i> (°)	102.090(10)	90	90.37(3)
<i>β</i> (°)	94.95(2)	91.850(10)	95.46(4)
<i>γ</i> (°)	75.670(10)	90	68.56(2)
<i>U</i> (Å <sup>3</sup> )	1478.5(4)	2919.9(10)	1575.9(10)
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$
<i>Z</i>	2	4	2
<i>D<sub>calc</sub></i> (Mg m <sup>-3</sup> )	2.352	2.377	2.594
Crystal size (mm)	0.25 × 0.25 × 0.20	0.45 × 0.34 × 0.17	0.15 × 0.10 × 0.10
Crystal habit	Red block	Orange-red plate	Green plate
<i>F</i> (000)	952	1896	1116
<i>μ</i> (mm <sup>-1</sup> )	12.985	13.149	13.183
Maximum, minimum relative transmission	1.00, 0.70	1.000, 0.194	0.998, 0.818
Data collection range (°)	3.17 < 2θ < 25.0	3.58 < 2θ < 25.0	2.59 < 2θ < 25.0
Index ranges (°)	0 ≤ <i>h</i> ≤ 14, -18 ≤ <i>k</i> ≤ 18, 0 ≤ <i>l</i> ≤ 19	-11 ≤ <i>h</i> ≤ 11, -1 ≤ <i>k</i> ≤ 25, -17 ≤ <i>l</i> ≤ 17	0 ≤ <i>h</i> ≤ 15, -15 ≤ <i>k</i> ≤ 16, -11 ≤ <i>l</i> ≤ 11
Reflections measured	2807	10 732	5816
Independent reflections	2791 ( <i>R<sub>int</sub></i> = 0.0246)	5104 ( <i>R<sub>int</sub></i> = 0.0855)	5542 ( <i>R<sub>int</sub></i> = 0.0396)
Refined parameters	188	267	389
<i>wR<sub>2</sub></i> (all data) <sup>2</sup>	0.2436	0.1011	0.0204
<i>x, y</i> <sup>2</sup>	0.0817, 10.458	0.0332, 0.0	0.0500, 7.765
<i>R<sub>1</sub></i> [ <i>I</i> > 2σ( <i>I</i> )] <sup>2</sup>	0.0480	0.0464	0.0455
Observed reflections	2321	3175	3848
Goodness-of-fit on <i>F</i> <sup>2</sup> (all data)	1.084	0.981	1.027
Maximum shift (σ)	0.03	0.01	0.04
Extinction coefficient		0.00156(8)	
Peak, hole in final difference map (e Å <sup>-3</sup> )	1.234, -1.390	1.124, -1.235	2.848, -1.307

<sup>1</sup> Data in common: graphite monochromated Mo-K<sub>α</sub> radiation, λ = 0.71073 Å, *T* = 293(2) K.

<sup>2</sup> *R*<sub>1</sub> = Σ(|*F<sub>o</sub>*| - |*F<sub>c</sub>*|) / Σ|*F<sub>o</sub>*|, *wR*<sub>2</sub> = [Σ*w*(*F<sub>o</sub>*<sup>2</sup> - *F<sub>c</sub>*<sup>2</sup>)<sup>2</sup> / Σ*wF<sub>c</sub>*<sup>4</sup>]<sup>1/2</sup>, *w* = 1 / [σ<sup>2</sup>(*F<sub>o</sub>*)<sup>2</sup> + (*xP*)<sup>2</sup> + *yP*], *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>) / 3, where *x* and *y* are constants adjusted by the program; goodness-of-fit = [Σ*w*(*F<sub>o</sub>*<sup>2</sup> - *F<sub>c</sub>*<sup>2</sup>)<sup>2</sup> / (*n* - *p*)]<sup>1/2</sup> where *n* is the number of reflections and *p* is the number of parameters.

tions measured at hourly intervals showed no significant variation in intensity. Cell parameters were obtained by least-squares refinement on diffractometer angles from 25 centred reflections (20 < 2θ < 25°) [17]. Semi-empirical absorption correction based on ψ-scan data were applied [18]. The structures were solved by direct methods (heavy atom positions) and subsequent Fourier difference syntheses (SHELXTL PLUS [19]) and refined anisotropically on all non-H atoms (**2**, **5**), or Os and Si atoms (**1**) by full-matrix least-squares on *F*<sup>2</sup> (SHELXL-93 [20]). Hydrogen atoms were placed in idealised positions and refined using a riding model or as rigid methyl groups. In the final cycles of refinement a weighting schemes were introduced which produced a flat analyses of variance. Crystal data and refinement details are given in Table 4.

#### 4. Supplementary material

Crystallographic data (excluding structure factors) for the structures **1**, **2** and **5** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 139906, 139907 and 139905, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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