



# Reaction of the diyne complex $[\text{Os}_3(\mu\text{-CO})(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-Me}_3\text{SiCCC}\equiv\text{CSiMe}_3\}]$ with phosphines and phosphites: Characterization of monophosphine substituted clusters $[\text{Os}_3(\mu\text{-CO})(\text{CO})_8(\text{PR}_3)\{\mu_3\text{-}\eta^2\text{-Me}_3\text{SiCCC}\equiv\text{CSiMe}_3\}]$ ( $\text{PR}_3 = \text{PPh}_3, \text{P}(\text{OEt})_3, \text{PEt}_3, \text{PPh}_2$ and $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ )

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## ARTICLE INFO

### Article history:

Received 29 July 2009

Received in revised form 15 October 2009

Accepted 16 October 2009

Available online 25 October 2009

### Keywords:

Osmium cluster carbonyl

Diyne

Phosphine

Phosphite

X-ray crystallography

## ABSTRACT

The reactions of  $[\text{Os}_3(\mu\text{-CO})(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-Me}_3\text{SiCCC}\equiv\text{CSiMe}_3\}]$  with phosphorus donor ligands ( $\text{PPh}_3, \text{PEt}_3, \text{P}(\text{OEt})_3, \text{PPh}_2$  and a diphosphine;  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm)) afford carbonyl mono-substitution products  $[\text{Os}_3(\mu\text{-CO})(\text{CO})_8(\text{L})\{\mu_3\text{-}\eta^2\text{-Me}_3\text{SiCCC}\equiv\text{CSiMe}_3\}]$  even in the case of the bidentate phosphine dppm. All the complexes have been characterized by IR and multinuclear NMR spectroscopy and for **2** ( $\text{L} = \text{PPh}_3$ ), **3** ( $\text{L} = \text{PEt}_3$ ), **4** ( $\text{L} = \text{P}(\text{OEt})_3$ ) and **5** ( $\text{L} = \eta^1\text{-dppm}$ ) the structures have been confirmed by single-crystal X-ray analysis. The structural analyses show that in all four clusters the substitution has occurred at one of osmium equatorial sites that is  $\sigma$ -bonded to the  $\mu_3\text{-}\eta^2$ -alkyne.

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## 1. Introduction

There has been an ongoing interest in the reactions between transition metal carbonyl clusters and hydrocarbon containing ligands for the last four decades because of the range of coordination modes that are adopted by the organic groups and by the possibility of both ligand rearrangements on the cluster core and cluster build up processes [1]. Alkynes and diynes, as ligands, in ruthenium and osmium cluster chemistry are particularly interesting because of the versatility of their chemistry that leads to a range of products involving carbon–carbon bond formation, carbonyl insertion and a range of hydrogenated products depending on whether  $[\text{M}_3(\text{CO})_{12}]$  ( $\text{M} = \text{Ru}, \text{Os}$ ),  $[\text{M}_3(\text{CO})_{10}(\text{NCMe})_2]$  or  $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$  is used as the cluster starting material [2]. Despite the plethora of cluster carbonyl complexes that contain diynes or their derivatives relatively little reaction chemistry has been carried out on the substituted complexes despite the presence of the diyne apparently activating the complex by comparison to the binary carbonyls [3–7]. In reported reactions of diyne-substituted cluster complexes decarbonylation as well as ligand rearrangement paths can occur. In addition, in clusters where a free alkyne moiety is present, there is the possibility of carrying out further reactions with this fragment, as exemplified by the reaction of  $[\text{Os}_3(\mu\text{-CO})(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-HC}_2\text{C}\equiv\text{CSiMe}_3\}]$  with  $[\text{Co}_2(\text{CO})_8]$  where the complex  $[\text{Os}_3(\mu\text{-CO})(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-HC}_2\text{C}_2\text{SiMe}_3\}\{\text{Co}_2(\text{CO})_6\}]$  was formed by coordination of the dicobalt fragment to the  $\text{C}\equiv\text{C}$  triple bond adjacent to the  $\text{SiMe}_3$  group [8]. When the ruthenium complex is used, a bow-tie cluster is formed by the insertion of the cobalt species into a  $\text{Ru}\text{--}\text{Ru}$  bond [9].

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We have recently observed the facile cleavage of C–Si bonds in trinuclear-acetylide derivatives [11]. This led us to explore the reactivity of  $[\text{Os}_3(\mu\text{-CO})(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-Me}_3\text{SiCC}\equiv\text{CSiMe}_3\}]$ ; **1** (Scheme 1); where there are two different C–Si bonds adjacent to the coordinated and uncoordinated alkyne groups, respectively. In this paper we report the reaction of compound **1** with several phosphines and a phosphite and show that, in all cases, mono-substitution of a carbonyl group in the plane of the  $\text{Os}_3$  triangle occurs and that the diyne group does have an influence on the rate of substitution, preventing coordination of bulky phosphines, but not on the position of substitution.

## 2. Results and discussion

The reactions of  $[\text{Os}_3(\mu\text{-CO})(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-Me}_3\text{SiCC}\equiv\text{CSiMe}_3\}]$  **1** with a series of phosphines and phosphites in hexane, under reflux, affords as the only products that could be isolated, the clusters  $[\text{Os}_3(\mu\text{-CO})(\text{CO})_8(\text{L})\{\mu_3\text{-}\eta^2\text{-Me}_3\text{SiCC}\equiv\text{CSiMe}_3\}]$  (**2**,  $\text{L} = \text{PPh}_3$ , **3**,  $\text{L} = \text{PEt}_3$ , **4**,  $\text{L} = \text{P}(\text{OEt})_3$ , **5**,  $\text{L} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm) and **6**,  $\text{L} = \text{PPhPh}_2$ ) where substitution of a carbonyl group took place. Reactions with other, bulkier phosphines ( $\text{PCy}_3$  and bis(dicyclohexylphosphino)ethane) [12] were also carried out. Interestingly, for these only unreacted starting material was recovered, even after prolonged heating, indicating that steric factors were important in the reaction pathway. However, the basicity of the phosphine [13] may also play a role. In the reaction with the most basic and the sterically least demanding phosphine,  $\text{PEt}_3$  in the series, the starting material is consumed most quickly. Since all the reactions were carried out for the same period of time, the yields of the mono-substituted products obtained under similar conditions, given in the Section 4, may reflect the rate of reaction. These results are in general agreement with the work of Poë et al. on the kinetics of associative reactions of metal carbonyl clusters [14]. Spectroscopic data for **2–6** is consistent with the presence of both the phosphine/phosphite and the diyne ligands in the reaction products. The similarity of the IR spectra, in the carbonyl region, of all the complexes suggests the symmetry and distribution of the carbonyl groups is similar for all of them. All the IR spectra have a signal below  $1900\text{ cm}^{-1}$  consistent with the fact that the bridging carbonyl group in **1** [15] is retained in the products.  $^1\text{H}$  NMR spectra for the five compounds **2–6**, show the  $\text{SiMe}_3$  signals, at similar values than in **1** [15], as well as those corresponding to the groups bonded to the phosphorus centres. The spectrum of **5** shows two doublets of doublets in the methylene region, indicating that the two hydrogen atoms in the  $\text{CH}_2$  group of the dppm ligand are not equivalent.

$^{31}\text{P}$  NMR spectra of **2–6** show the shift of the signals to higher frequencies than those observed in the free phosphine with the

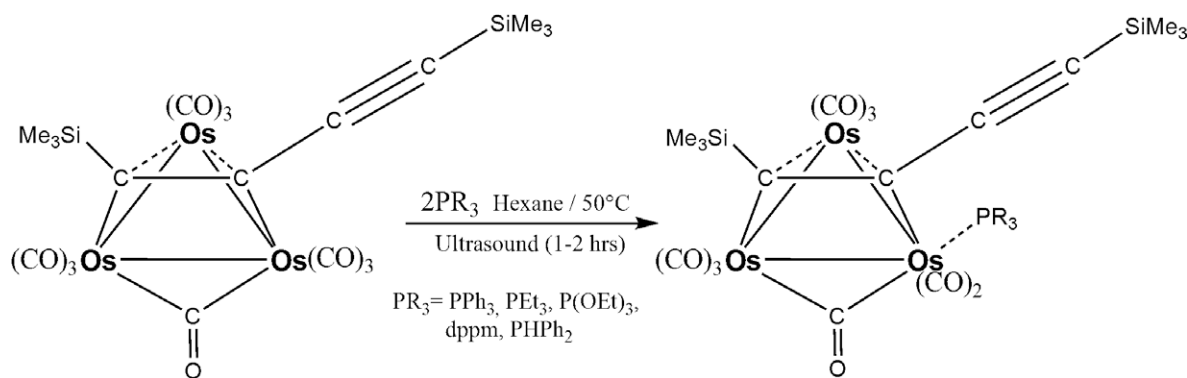
exception of the case of the  $\text{P}(\text{OEt})_3$  ligand which moves to lower frequency. This behavior is similar to that observed in other complexes of these ligands although the effect is less marked in other cases such as  $[\text{Os}_3(\text{CO})_{11}(\text{PPh}_3)]$  where there is a  $\Delta\delta$  shift of free phosphine to coordinated phosphine of only  $+2.74$  ppm in comparison to  $+18.42$  ppm in **2** [16]. In the case of compound **5**, the spectrum shows two singlets; one at  $2.79$  ppm, which is assigned to the coordinated  $\text{PPh}_2$  group, and another one at  $-26.37$  ppm, more similar to the value of the free phosphine ( $-21.24$  ppm), assigned to a non-coordinated phosphorus centre.

The  $^{13}\text{C}$  NMR spectra of compounds **2–5** were obtained. The corresponding spectrum for compound **1** had not been reported but we also obtained it; signals are observed in  $125.10$  ppm for C(1), in  $139.43$  ppm for C(2), in  $117.84$  ppm for C(3) and in  $100.15$  ppm for C(4).

The assignment of the different signals of compounds **2–5** was thus made by comparison with the spectrum of **1** as well as the shifts observed for  $[\text{Os}_3(\text{CO})_{10}(\text{HC}\equiv\text{CSiMe}_3)]$  [17] and  $\text{Mo}_2(\mu\eta^2\text{-Me}_3\text{SiC}_2\text{C}\equiv\text{CSiMe}_3)(\text{CO})_4(\text{Cp})_2$  [18]. The signals observed between  $120$  and  $127$  ppm in the four compounds, are assigned to C(1), the terminal carbon atom of the coordinated alkyne moiety while the signals between  $157$  and  $160$  ppm are assigned to C(2), the other carbon atom of the coordinated alkyne. C(3) is believed to show signals between  $113$  and  $117$  ppm while C(4) shows signals at slightly lower frequencies  $93$  ppm; these last two carbon atoms were assigned to the alkyne that is not coordinated to the cluster, by comparison with the trends observed in the experimental spectrum of the free ligand in which C(1) and C(4) are observed at  $86.00$  ppm and C(2) and C(3) are observed at  $88.05$  ppm. The very similar chemical shifts of the carbon atoms in the organic chains in compound **2–5** indicate that the electronic properties of the diyne group are not significantly affected by the variation of the phosphine or phosphite ligand.

X-ray crystal structures of compounds **2–5** were obtained and the molecular structures are shown in Figs. 1–4, respectively, while some selected bond lengths and angles are given in Table 1. The four structures show that, as proposed, substitution of one carbonyl group by a phosphine or phosphite group occurred, even in the case of the bidentate phosphine dppm where one of the phosphorus atoms remains uncoordinated. Apart from **3**, where there are two independent but structurally similar molecules in the asymmetric unit, each structure crystallizes with one independent molecule in the asymmetric unit. There are no short intermolecular contacts and the molecules within the crystal are separated by normal van der Waals distances.

The overall core geometry in each structure is very similar and reminiscent of that in the parent cluster **1** and the related species  $[\text{Os}_3(\mu\text{-CO})(\text{CO})_9\{\mu_3\text{-}\eta^2\text{-PhCC}\equiv\text{CPh}\}]$  [19]. In each structure **2–5** the osmium atoms form an isosceles triangle the longest edge of



Scheme 1.

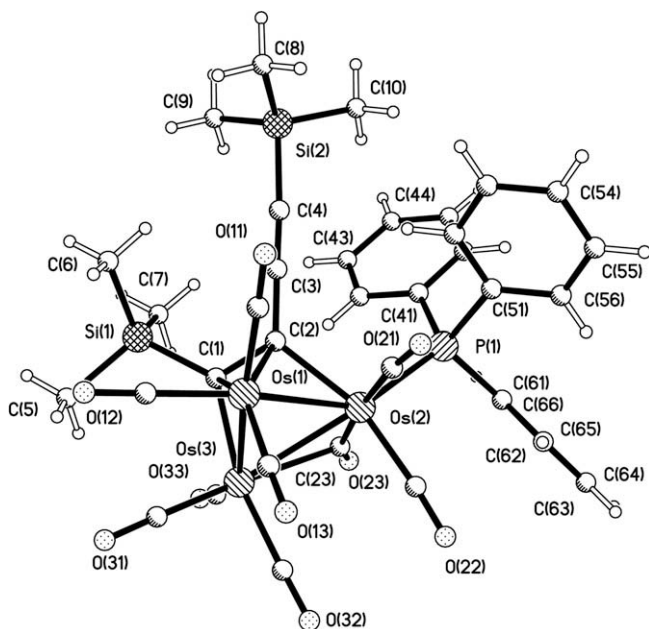


Fig. 1. The molecular structure of **2** showing the atom numbering scheme adopted.

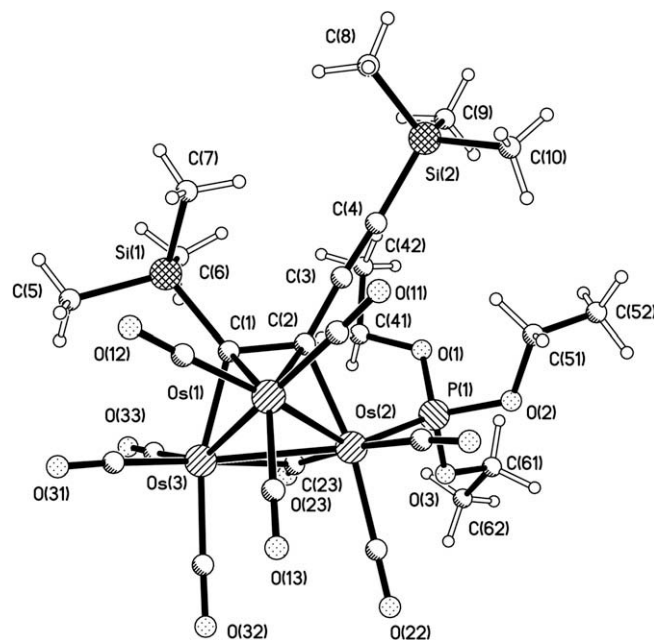


Fig. 3. The molecular structure of **4** showing the atom numbering scheme adopted.

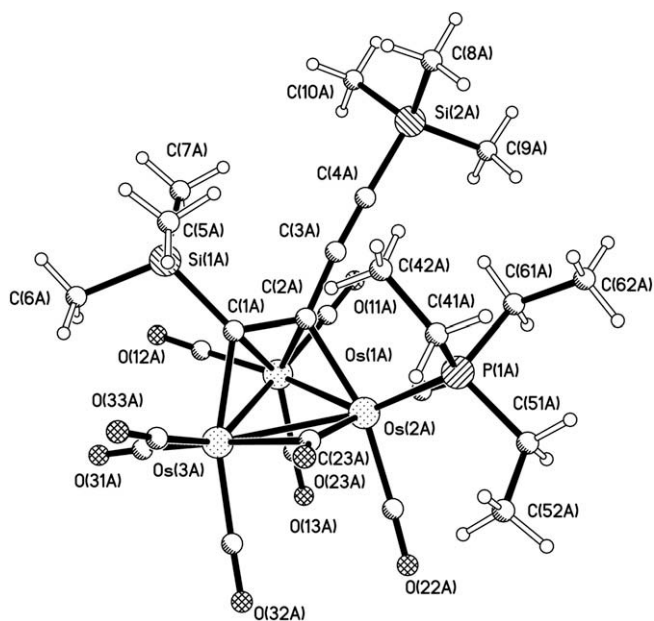


Fig. 2. One of the two independent but structurally similar molecules of **3** showing the atom numbering scheme adopted.

which, Os(2)–Os(3), is parallel to the coordinated alkyne bond, C(1)–C(2), and bridged by a carbonyl ligand. The other eight carbonyl ligands are terminal, three in axial sites and five in equatorial sites. As in a range of alkyne clusters [20] the coordinated alkyne group is  $\sigma$ -bonded to Os(2) and Os(3) and  $\pi$ -bonded to Os(1) in a conventional  $\parallel$ -bonding mode with the C(1)–C(2) distances ranging from 1.420(6) to 1.435(10) Å, while the uncoordinated alkyne groups in the diyne have C(3)–C(4) distances in the range 1.195(10)–1.219(10) Å as expected for a C $\equiv$ C triple bond. Within the diyne the uncoordinated component is essentially linear.

The main structural difference between **1** and **2–5** is obviously the replacement of an equatorial carbonyl by the phosphorus donor ligand. In the four clusters **2–5** the phosphorus donor ligand

bonds to the osmium atom, Os(2), that is also  $\sigma$ -bonded to C(2), the carbon atom of the coordinated alkyne group that is also attached to the free alkyne unit,  $\text{--C}\equiv\text{CSiMe}_3$ . This is the least sterically crowded of the equatorial sites on Os(2) and Os(3) and the trimethylsilyl group attached to the uncoordinated alkyne bond fits in the cleft of two of the phenyl rings of the PPh<sub>3</sub> group. If the phosphorus donor occupied the equivalent site on Os(3) there would be a steric clash between the phosphorus substituents and the SiMe<sub>3</sub> group bonded to C(1) of the coordinated alkyne. On closer inspection of each of the structures it is apparent that the phosphorus donor ligand lies in a *pseudo*-equatorial position somewhat displaced towards the same side of the Os<sub>3</sub> plane as the diyne ligand. For **2** P(1) is 0.95 Å above the Os<sub>3</sub> plane, while for **3**, **4** and **5**, the equivalent distances are 1.07 and 1.12 Å (two independent molecules), 1.07 Å and 1.09 Å, respectively. This, presumably, reduces the steric interactions between the phosphorus donor ligands and the carbonyl groups on Os(2). The Os(1)–Os(2)–P(1) and Os(3)–Os(2)–P(1) angles lie in the range 136.82(5)–144.48(5)° which indicates that the phosphorus atom is not close to being *trans* to either of the Os–Os bonds or to the Os(2)–C(2) bond (if the phosphorus donor ligand were to occupy a *pseudo*-axial position) as has been observed in phosphine-substituted triosmium alkyne clusters [21] but the P(1)–Os(2) vector almost bisects the Os(3)–Os(2)–Os(1) angle. The Os–P(phosphine) bond lengths lie in the range 2.367(2)–2.379(2) Å while the Os–P(phosphite) bond length in **4** is a little shorter at 2.3010(16) Å. This is a similar trend observed to that in a range of triruthenium and triosmium phosphine and phosphite-substituted clusters [21,22] and reflects the difference in the donor and acceptor properties of phosphines and phosphites. It is also worthy of note that Os–P distances are slightly longer in **2** and **3**, than in the simple substituted phosphine complex [Os<sub>3</sub>(CO)<sub>11</sub>(PR<sub>3</sub>)] [23]. The same trend is observed when the Os–P distance of the  $\eta^1$ -dppm ligand in [Os<sub>3</sub>(CO)<sub>9</sub>( $\mu$ -dppm)( $\eta^1$ -dppm)] is compared with the corresponding value in **5** [24]. This lengthening could be the result of the steric effect induced by the alkyne coordination. The presence of the phosphorus donor seems to have little effect on the coordination of the diyne. The  $\pi$ -bonding involving Os(1) and C(1) and C(2) shows a small but hardly significant asymmetry with the Os(1)–C(1)

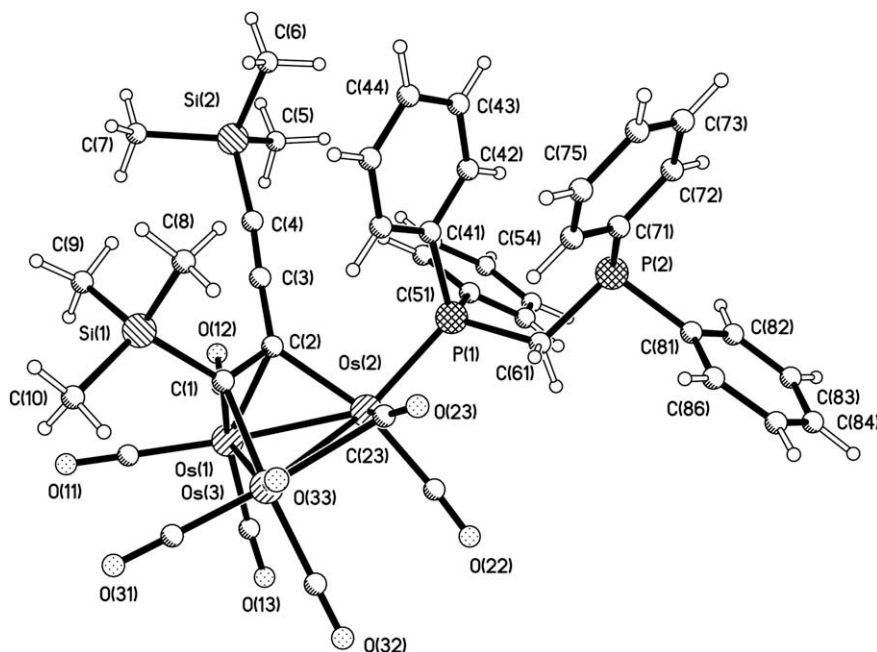


Fig. 4. The molecular structure of **5** showing the atom numbering scheme adopted.

Table 1

Some selected bond lengths (Å) and angles (°) for compounds **2–5**.

Compounds	<b>2</b>	<b>3<sup>a</sup></b>	<b>4</b>	<b>5</b>
Os(1)–Os(2)	2.7837(2)	2.7825(4), 2.7846(4)	2.7877(3)	2.7851(4)
Os(1)–Os(3)	2.7367(2)	2.7418(4), 2.7452(4)	2.7437(3)	2.7388(5)
Os(2)–Os(3)	2.8555(3)	2.8467(4), 2.8426(3)	2.8439(3)	2.8513(4)
Os(1)–C(1)	2.273(4)	2.273(7), 2.272(6)	2.261(6)	2.367(2)
Os(1)–C(2)	2.234(4)	2.254(6), 2.243(6)	2.251(6)	2.231(7)
Os(2)–C(2)	2.139(4)	2.131(6), 2.115(7)	2.142(6)	2.144(7)
Os(3)–C(1)	2.129(5)	2.157(6), 2.137(7)	2.131(6)	2.118(7)
Os(2)–P(1)	2.3779(11)	2.379(2), 2.3736(18)	2.3010(16)	2.367(2)
Os(2)–C(23)	1.998(4)	2.020(7)2.024(7)	1.997(6)	1.958(9)
Os(3)–C(23)	2.516(5)	2.383(7)2.395(7)	2.430(6)	2.456(8)
C(1)–Si(1)	1.887(5)	1.881(7), 1.884(7)	1.901(6)	1.890(7)
C(4)–Si(2)	1.840(5)	1.834(7), 1.828(7)	1.831(7)	1.847(9)
C(1)–C(2)	1.420(6)	1.828(7), 1.433(9)	1.430(8)	1.435(10)
C(2)–C(3)	1.435(6)	1.424(10), 1.444(9)	1.427(8)	1.435(11)
C(3)–C(4)	1.204(6)	1.219(10), 1.195(10)	1.210(9)	1.208(12)
Si(1)–C(1)–C(2)	122.8(3)	124.4(5), 123.9(5)	123.9(4)	122.6(5)
C(1)–C(2)–C(3)	121.1(4)	123.8(6), 123.4(6)	124.4(5)	123.9(7)
C(2)–C(3)–C(4)	175.8(4)	175.4(8), 172.8(7)	176.4(7)	177.7(8)
C(3)–C(4)–Si(2)	173.9(4)	173.3(6), 173.2(6)	176.5(6)	175.0(8)
Os(1)–Os(2)–P(1)	143.31(2)	144.38(5), 143.44(5)	142.77(4)	142.01(5)
Os(3)–Os(2)–P(1)	143.29(3)		138.45(4)	139.87(5)

<sup>a</sup> There are two molecules in the asymmetric unit.

distances in the four structures being a little longer than the Os(1)–C(2) distances, and the variation is smaller than in the unsubstituted complex **1**, and the  $\sigma$ -bond between Os(2)–C(2) and Os(3)–C(1) show no discernable trends.

The bridging carbonyl group, C(23)–O(23), in all the structures exhibits a similar asymmetry to that observed in **1** (Os–C 2.013(12) and 2.486(15) Å, Os–C–Os 78.3(10)°), with the Os(2)–C(23) distances ranging from 1.997(6) in **4** to 2.025(9) Å in **5** and Os(3)–C(23) distances ranging from 2.383(2) in **3** to 2.516(5) Å in **1**. The Os(2)–C(23)–Os(3) angles lie in the range 77.54(14) in **1** to 80.1(2)° in **3**. Thus, the presence of the phosphorus donor ligand does not have a significant effect on the bonding parameters within the bridging carbonyl; Rosenberg, Gobetto and coworkers had

observed an increase in asymmetry of the bridging carbonyl in [Os<sub>3</sub>(CO)<sub>9</sub>(alkyne)L] derivatives [25].

### 3. Conclusions

Five new phosphine or phosphite-substituted clusters with the formula [Os<sub>3</sub>( $\mu$ -CO)(CO)<sub>8</sub>(L)]{ $\mu$ - $\eta^2$ -Me<sub>3</sub>SiC<sub>2</sub>C<sub>2</sub>SiMe<sub>3</sub>} (L = **2** PPh<sub>3</sub>; **3** PEt<sub>3</sub>; **4** P(OEt)<sub>3</sub>; **5**  $\eta^1$ -dppm; **6** PPh<sub>2</sub>) have been synthesized from [Os<sub>3</sub>( $\mu$ -CO)(CO)<sub>9</sub>]{ $\mu$ - $\eta^2$ -Me<sub>3</sub>SiCCC≡CSiMe<sub>3</sub>} **1**. The complexes have been fully characterized and it has been observed that the rate of formation of the complexes and the geometry adopted can be related to the bulk of the phosphorus donor group used,

with no reaction occurring when bulkier phosphines such as PCy<sub>3</sub> and bis(dicyclohexylphosphino)ethane are employed. Unlike, equivalent reactions with [Ru<sub>3</sub>(CO)<sub>12</sub>] and [Os<sub>3</sub>(CO)<sub>12</sub>] and other derivatives [1,2] the presence of the diyne favours the formation of the mono-substituted phosphines and phosphites and there is no evidence for di- or tri-substituted products. This provides greater control over the reactions and the mono-substituted products can be obtained in higher yield. The isolation, in good yield, of **5** and **6** means that cluster build-up reactions with other mono-metal and cluster fragments can be attempted by direct coordination to the free phosphorus donor site in **5** and by deprotonation of the PPh<sub>2</sub> group in **6**, and this work is currently in progress.

## 4. Experimental

### 4.1. General

The reagents used in this work [Os<sub>3</sub>(CO)<sub>12</sub>], PPh<sub>3</sub>, PEt<sub>3</sub>, P(OEt)<sub>3</sub>, dppm, PPh<sub>2</sub> and the diyne Me<sub>3</sub>SiCC≡CCSiMe<sub>3</sub> were purchased from Aldrich and were used without further purification. All reactions were carried out under a nitrogen atmosphere using dry solvents. Once isolated, the products were handled under atmospheric conditions which indicated their high stability. Infrared spectra were recorded on a Nicolet Nexus FT-IR spectrometer while NMR spectra were obtained on a 300 MHz Bruker spectrometer. High resolution mass spectra were obtained in a TOF Agilent G1969A with electrospray ionization.

### 4.2. Synthesis of compounds

Synthesis of [Os<sub>3</sub>(CO)<sub>10</sub>(Me<sub>3</sub>SiCC≡CCSiMe<sub>3</sub>)] (compound **1**). This compound was prepared using as starting material [Os<sub>3</sub>(CO)<sub>10</sub>(MeCN)<sub>2</sub>]; prepared as reported [26]; dissolved in a dichloromethane solution and stirred with two equivalents of the diyne at

room temperature for 1 h. After evaporation of the solvent under vacuum, the mixture is separated by TLC and compound **1** was separated and characterized by comparison with reported data [15].

#### 4.2.1. Reactions of compound **1** with phosphines and phosphites

Compound **1** was mixed with the corresponding phosphine or phosphite in 1:2 ratio, in hexane and placed in an ultrasound bath at 50 °C for periods of 1–2 h until disappearance of the free phosphine was confirmed by monitoring the reaction using <sup>31</sup>P NMR spectroscopy. Only mono-substitution products as well as the oxidized phosphine are detected in the corresponding spectra. The substitution products **2–6** were separated from some unreacted **1** by thin layer chromatography using hexane as eluent.

#### 4.2.2. Spectroscopic data for Me<sub>3</sub>SiC≡CC≡CSiMe<sub>3</sub>

NMR data: (in CDCl<sub>3</sub>, ppm): <sup>1</sup>H: 0.16 (s, SiMe<sub>3</sub>); <sup>13</sup>C: –0.42 (s, SiMe<sub>3</sub>), 86.00 [C(1), C(4)] and 88.05 [C(2), C(3)]; <sup>29</sup>Si: –15.44.

#### 4.2.3. Spectroscopic data for compound **1**

NMR data: (in CDCl<sub>3</sub>, ppm): <sup>1</sup>H: 0.10 (s, SiMe<sub>3</sub> coordinated alkyne), 0.16 (s, SiMe<sub>3</sub> non-coordinated alkyne); <sup>13</sup>C: 125.109 [(C1)], 139.433 [(C2)], 117.840 [(C3)] and 100.156 [(C4)]; <sup>29</sup>Si: 12.322 (SiMe<sub>3</sub> coordinated alkyne), –17.313 (SiMe<sub>3</sub> non-coordinated alkyne).

#### 4.2.4. Spectroscopic data for compound **2**

Yield: 57.6%. IR ν(CO) in hexane: 2109(w), 2077(s), 2041(vs), 2024(s), 2000(s), 1991(w), 1978(w), 1850(w) cm<sup>-1</sup>. NMR data: (in CDCl<sub>3</sub>, ppm): <sup>1</sup>H: 7.5–7.8 (Ph), –0.3, 0.15 (SiMe<sub>3</sub>); <sup>31</sup>P: 14.12; <sup>13</sup>C: 120.36 [C(1)], 157.97 [C(2)], 117.07 [C(3)], 93.8 [C(4)]; <sup>29</sup>Si: 9.81 (SiMe<sub>3</sub> coordinated alkyne), –19.02 (SiMe<sub>3</sub> non-coordinated alkyne). Mass spectrometry: +TOF MS [C<sub>37</sub>H<sub>34</sub>O<sub>9</sub>Si<sub>2</sub>POs<sub>3</sub>], *m/z* = 1285.0319 (exp.), 1285.0318 (calc.) *uma*, error: 0.0655 ppm.

**Table 2**  
Crystallographic data for compounds **2–5**.

	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Empirical formula	C <sub>37</sub> H <sub>33</sub> O <sub>9</sub> Os <sub>3</sub> PSi <sub>2</sub>	C <sub>25</sub> H <sub>33</sub> O <sub>9</sub> Os <sub>3</sub> PSi <sub>2</sub>	C <sub>25</sub> H <sub>33</sub> O <sub>12</sub> Os <sub>3</sub> PSi <sub>2</sub>	C <sub>44</sub> H <sub>40</sub> O <sub>9</sub> Os <sub>3</sub> P <sub>2</sub> Si <sub>2</sub>
Formula weight	1279.38	1135.26	1183.26	1401.48
Crystal size	0.25 × 0.25 × 0.15	0.30 × 0.15 × 0.10	0.25 × 0.25 × 0.10	0.30 × 0.20 × 0.20
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	P2 <sub>1</sub> /n	P1	P1	P1
Unit cell dimensions				
<i>a</i> (Å)	8.9040(1)	12.3390(1)	16.0270(1)	10.5020(2)
<i>b</i> (Å)	24.8530(2)	17.6990(2)	11.0940(1)	11.6200(2)
<i>c</i> (Å)	18.5110(2)	17.7630(2)	19.8910(1)	20.2980(5)
α (°)		63.143(1)		76.499(1)
β (°)	92.913(1)	83.109(1)	97.159(1)	80.053(1)
γ (°)		89.720(1)		77.479(1)
Volume (Å <sup>3</sup> )	4091.03(7)	3430.47(6)	3509.12(4)	2331.76(8)
<i>Z</i>	4	4	4	2
<i>D</i> <sub>calc</sub>	2.077	2.198	2.240	1.996
Absorption coefficient	9.442	11.244	11.003	8.325
<i>F</i> (0 0 0)	2392	2104	2200	1324
Temperature (K)	150(2)	150(2)	150(2)	150(2)
θ Range for collection	2.98–27.48	3.55–26.37	3.59–26.37	2.96–29.99
Index ranges	–11 ≤ <i>h</i> ≤ 11 –24 ≤ <i>k</i> ≤ 32 –24 ≤ <i>l</i> ≤ 24	–15 ≤ <i>h</i> ≤ 15 22 ≤ <i>k</i> ≤ 22 –22 ≤ <i>l</i> ≤ 22–	–20 ≤ <i>h</i> ≤ 20 –13 ≤ <i>k</i> ≤ 13 –24 ≤ <i>l</i> ≤ 24	–14 ≤ <i>h</i> ≤ 14 –15 ≤ <i>k</i> ≤ 16 –27 ≤ <i>l</i> ≤ 28
Reflections collected	42576	55912	62221	35002
Independent reflections ( <i>R</i> <sub>int</sub> )	9379 [0.0961]	13980 [0.0849]	7154 [0.1571]	13279 [0.1150]
Maximum and minimum transmission	0.326 and 0.216	0.609 and 0.359	0.587 and 0.196	0.2868 and 0.1891
Data/restraints/parameters	9379/0/475	13980/0/739	7154/0/397	13279/0/547
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0295, <i>wR</i> <sub>2</sub> = 0.0715	<i>R</i> <sub>1</sub> = 0.0391, <i>wR</i> <sub>2</sub> = 0.0977	<i>R</i> <sub>1</sub> = 0.0427, <i>wR</i> <sub>2</sub> = 0.1145	<i>R</i> <sub>1</sub> = 0.0559, <i>wR</i> <sub>2</sub> = 0.1259
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0373, <i>wR</i> <sub>2</sub> = 0.0758	<i>R</i> <sub>1</sub> = 0.0476, <i>wR</i> <sub>2</sub> = 0.1035	<i>R</i> <sub>1</sub> = 0.0463, <i>wR</i> <sub>2</sub> = 0.1178	<i>R</i> <sub>1</sub> = 0.0953, <i>wR</i> <sub>2</sub> = 0.1402
Goodness-of-fit (GOF)	1.087	1.041	1.037	0.994
Maximum, minimum peaks (e Å <sup>-3</sup> )	1.127 and –2.820	2.767 and –2.759	4.220 and –2.789	3.136 and –4.815

#### 4.2.5. Spectroscopic data for compound 3

Yield: 87.3%. IR  $\nu(\text{CO})$  in hexane: 2109(w), 2077(s), 2041(vs), 2016(s), 1999(s), 1991(w), 1978(w), 1850(w)  $\text{cm}^{-1}$ . NMR data: (in  $\text{CDCl}_3$ , ppm):  $^1\text{H}$ : 2.2 ( $\text{CH}_2$ ,  $\text{PEt}_3$ ) and 1.05 ( $\text{CH}_3$ ,  $\text{PEt}_3$ ),  $-0.01$ ,  $0.01$  ( $\text{SiMe}_3$ ),  $^{31}\text{P}$ : 4.10;  $^{13}\text{C}$ : 120.66 [C(1)], 160.14 [C(2)], 113.3 [C(3)], 93.21 [C(4)];  $^{29}\text{Si}$ : 9.04 ( $\text{SiMe}_3$  coordinated alkyne),  $-18.47$  ( $\text{SiMe}_3$  non-coordinated alkyne). Mass spectrometry: +TOF MS [ $\text{C}_{25}\text{H}_{34}\text{O}_9\text{Si}_2\text{PO}_3$ ],  $m/z = 1141.0323$  (exp.), 1141.0318 (calc.) uma, error:  $-0.6272$  ppm.

#### 4.2.6. Spectroscopic data for compound 4

Yield: 43.8%. IR  $\nu(\text{CO})$  in hexane: 2109(w), 2080(s), 2043(vs), 2032(s), 2000(s), 1994(w), 1981(w), 1850(w)  $\text{cm}^{-1}$ . NMR data: (in  $\text{CDCl}_3$ , ppm):  $^1\text{H}$ : 4.0 ( $\text{CH}_2$ ,  $\text{P}(\text{OEt})_3$ ), 1.25 ( $\text{CH}_3$ ,  $\text{P}(\text{OEt})_3$ ), 0.01 ( $\text{SiMe}_3$ );  $^{31}\text{P}$ : 99.97;  $^{13}\text{C}$ : 120.5 [C(1)], 158.31 [C(2)], 115.25 [C(3)], 93.2 [C(4)];  $^{29}\text{Si}$ : 9.69 ( $\text{SiMe}_3$  coordinated alkyne),  $-18.77$  ( $\text{SiMe}_3$  non-coordinated alkyne). Mass spectrometry: +TOF MS [ $\text{C}_{25}\text{H}_{34}\text{O}_{12}\text{Si}_2\text{PO}_3$ ],  $m/z = 1189.0145$  (exp.), 1189.0165 (calc.) uma, error:  $-1.7322$  ppm.

#### 4.2.7. Spectroscopic data for compound 5

Yield: 68.7%. IR  $\nu(\text{CO})$  in  $\text{CH}_2\text{Cl}_2$ : 2101(vw), 2076(s), 2040(vs), 2030(s), 1999(s), 1978(w), 1848(vw)  $\text{cm}^{-1}$ . NMR data: (in  $\text{CDCl}_3$ , ppm):  $^1\text{H}$ : 3.5 (1H,  $\text{CH}_2$ ), 4.1 (1H,  $\text{CH}_2$ ), 7.3–7.8 (Ph), 0.025, 0.035 ( $\text{SiMe}_3$ );  $^{31}\text{P}$ : 2.79 (coordinated  $\text{PPh}_2$ ),  $-26.37$  (non-coordinated  $\text{PPh}_2$ );  $^{13}\text{C}$ : 127.33 [C(1)], 160.81 [C(2)], 117.59 [C(3)], 94.95 [C(4)];  $^{29}\text{Si}$ : 9.36 ( $\text{SiMe}_3$  coordinated alkyne),  $-18.98$  ( $\text{SiMe}_3$  non-coordinated alkyne). Mass spectrometry: +TOF MS [ $\text{C}^{44}\text{H}_{41}\text{O}_9\text{Si}_2\text{PO}_3$ ],  $m/z = 1407.0606$  (exp.), 1407.0603 (calc.) uma, error: 0.1745 ppm.

#### 4.2.8. Spectroscopic data for compound 6

Yield: 36.9%. IR  $\nu(\text{CO})$  in hexane 2109(vw), 2078(s), 2042(vs), 2025(s), 2000(s), 1991(w), 1980(w), 1895(vw)  $\text{cm}^{-1}$ . NMR data: (in  $\text{CDCl}_3$ , ppm):  $^1\text{H}$ : 6.25 (PH), 7.4–7.7 (Ph), 0.01 ( $\text{SiMe}_3$ );  $^{31}\text{P}$ : 1.69;  $^{29}\text{Si}$ : 9.27 ( $\text{SiMe}_3$  coordinated alkyne),  $-19.07$  ( $\text{SiMe}_3$  non-coordinated alkyne). Mass spectrometry: +TOF MS [ $\text{C}_{31}\text{H}_{30}\text{O}_9\text{Si}_2\text{PO}_3$ ],  $m/z = 1209.0035$  (exp.), 1209.0005 (calc.) uma, error: 2.4684 ppm.

#### 4.3. X-ray crystallography

Single crystals of compounds **2–5** were obtained from dichloromethane–hexane solutions. Crystal data and details of the structures are listed in Table 2. Data for compounds **2–5** were collected in a Bruker Kappa CCD diffractometer, at 150(2) K, using graphite monochromated Mo  $\text{K}\alpha$  radiation and  $2^\circ$   $\omega$  scans. The structures were solved using direct methods (SIR 92 [27]) and refined using full-matrix least-squares on  $F^2$ . All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms in the methyl, methylene and phenyl groups were fixed at idealized positions and were allowed to ride on the relevant carbon atoms; displacement parameters were set at 1.2 times that of the carbon atoms for the phenyl and methylene hydrogen atoms and at 1.5 times that of the carbon atoms for the methyl hydrogen atoms. In the final cycles of refinement weighting schemes were introduced that gave a relatively flat analysis of variance. Refinement continued until convergence was reached. All refinements were carried out using the SHELXL-97 package [28].

#### Acknowledgments

I.T.S. thanks CONACYT for the award of a scholarship and the support to visit the University of Bath. We are also grateful to the Consejo Superior de Investigaciones Científicas de España for

the award of a licence of the Cambridge Crystallographic Data Base. S.K.B. is grateful to the University of Bath for support and P.R.R. wishes to thank the EPSRC for a Senior Research Fellowship. We thank Vianney González-López and Géiser Cuéllar-Rivera for obtention of mass spectra and Víctor González for his help in the acquisition of NMR data.

#### Appendix A. Supplementary material

CCDC 739076, 739077, 739078 and 739079 contain the supplementary crystallographic data for compounds **2**, **3**, **4** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.018.

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