

The photochemical and thermal reactions of a triosmium cluster carrying a γ -pyrone ligand with alkynes [☆]

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Abstract

The reaction of the cluster $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)$ (**1**) with a number of alkynes under thermal or visible light irradiation conditions, afforded in most cases the dinuclear complexes $\text{Os}_2(\text{CO})_6(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu\text{-LH})$ ($\text{L} = \text{PhCCPh}$, tBuCCH , tBuCCMe or EtCCEt) (**2**) or the trinuclear chain complexes $\text{Os}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu\text{-RCCHC}_6\text{H}_4)$ ($\text{R} = \text{H}$, Ph) (**3**). In the case of PhCCPh , a new isomer of $\text{Os}_3(\text{CO})_8(\text{PhCCPh})_2$, viz., $\text{Os}_3(\text{CO})_8(\mu\text{-PhCCPh})(\mu\text{-PhCCHC}_6\text{H}_4)$ (**7**) has been isolated and characterised.

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1. Introduction

The reactivity of clusters carrying a ligand other than carbonyl or hydride continues to be of great interest. These additional ligands may act as ancillary ligands to stabilise and affect the reactivity of the cluster [1], or may themselves act as substrates for reaction with the alkynes [2]. Thus in the triiron and triruthenium μ_3 -phenylimido clusters $\text{M}_3(\mu_3\text{-NPh})_2(\text{CO})_9$ and $\text{H}_2\text{M}_3(\mu_3\text{-NPh})(\text{CO})_9$ ($\text{M} = \text{Fe}$, Ru), reactions with alkynes generally led to dinuclear complexes for the iron analogues and tetranuclear complexes for the ruthenium analogues [2a]. In the iminium-bridged triosmium cluster $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-H}_2\text{CNMe}_2)$, the reaction with DMAD led to trinuclear products, both with triangular arrangement as well as an open chain, of the osmium core. However, it is clear that the reactivity in this case is driven primarily by the active CH_2 group on the iminium, leading to C–C coupling and/or rearrangement of the iminium [2b]. In the imido triruthenium and triosmium systems $\text{Ru}_3(\mu_3\text{-MeC}=\text{N}(\text{Et}))(\mu\text{-H})$ and $\text{M}_3(\mu_3\text{-C}=\text{N}(\text{CH}_2)_3)(\text{CO})_9$ that have been extensively investigated by Rosenberg and coworkers,

the reactions with alkynes proceed with retention of the triangulo trinuclear framework, with the exception of the reaction with DMAD (which gave an open chain product) and the reaction of the triruthenium with 2-butyne (which gave also a diruthenium product) [1a].

In an earlier paper, we have reported our investigations into the binding of pyrones onto a triosmium cluster [3]. The simple pyrones generally bind to the triosmium framework via the exocyclic oxygen and an orthometallation, for example, γ -pyrone gave the cluster $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)$ (**1**). These clusters are among a very few triosmium clusters known that contain an O-heterocycle [4], and unlike the clusters involving N-donor ligands mentioned above, the reactivity of this class of clusters has not been studied to any great extent. Furthermore, pyrones are known to exhibit interesting photochemistry, for instance, photochemical activation of γ -pyrone can result in rearrangement and intramolecular [2 + 2] cycloaddition reactions [5]. We were therefore interested to study the reactivity of cluster **1**, and our investigations into its reactivity with alkynes is reported here.

2. Results and discussion

Cluster **1** is thermally and photochemically quite stable; refluxing a toluene solution or photolysis

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with UV or visible light led to the recovery of unreacted **1**.

2.1. Reactions with $\text{PhC}\equiv\text{CPh}$

Irradiation of a cyclohexane solution of **1** and excess PhCCPh with a tungsten lamp for 2 d afforded four products, viz., the novel complexes $\text{Os}_2(\text{CO})_6(\mu-\gamma-\text{C}_5\text{H}_3\text{O}_2)(\mu-\text{PhCCHPh})$ (**2a**) and $\text{Os}_3(\text{CO})_9(\mu-\text{H})(\mu-\gamma-\text{C}_5\text{H}_3\text{O}_2)(\mu-\text{PhCCHC}_6\text{H}_4)$ (**3a**) and the previously known clusters $\text{Os}_3(\text{CO})_8(\text{PhCCPh})_2$ (**4**) and $\text{Os}_3(\text{CO})_9-(\text{PhCCPh})_2$ (**5**)

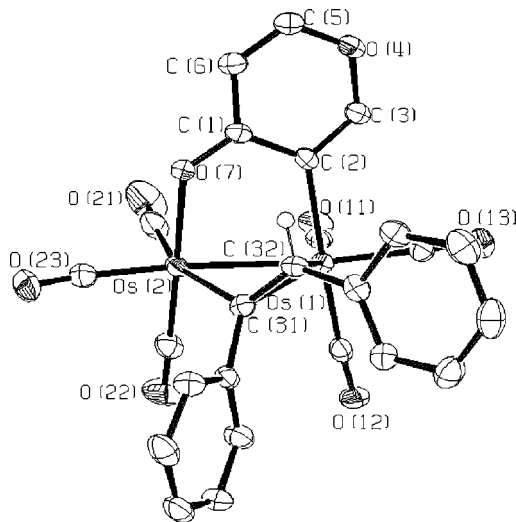


Fig. 1. ORTEP diagram of **2a** (50% probability thermal ellipsoids; aromatic and pyrone hydrogens omitted).

[6,7]. Both **2a** and **3a** have been characterised by single crystal X-ray crystallographic studies; their ORTEP diagrams are given in Figs. 1 and 2, respectively.

Interestingly, when the photolysis was carried out by maintaining the reaction vessel at 10 °C over a similar period of time, only **3a** was isolated, in 12% yield. Photolysis of **3a** also did not afford **2a**. The results of the photochemical reactions are summarised in Scheme 1.

When **1** was heated with two equivalents of PhCCPh at 100 °C, three major cluster products were isolated, together with hexaphenylbenzene. The cluster products were the two previously reported clusters **4** and $\text{Os}_3(\text{CO})_8(\mu-\text{H})(\mu-\text{PhCCPhCPhCC}_6\text{H}_4)$ (**6**) [8], and a novel red cluster $\text{Os}_3(\text{CO})_8(\mu-\text{PhCCPh})(\mu-\text{PhCCHC}_6\text{H}_4)$ (**7**). Trace amounts of **5** and another known cluster, $\text{Os}_3(\text{CO})_7(\text{PhCCPh})_3$ (**8**) were also identified spectroscopically. Single crystal X-ray crystallographic studies have been carried out on **6** and **7**. The single crystal X-ray structure of **6** has already been reported earlier [8a]; the one characterised here is a dichloromethane solvate and the structural features are essentially similar. The ORTEP diagram of **7**, together with selected bond parameters, is given in Fig. 3.

Cluster **7** was not among the products in the original report on the thermal reaction between $\text{Os}_3(\text{CO})_{12}$ and PhCCPh [7]. Its structure shows that one of the alkyne ligand is orthometallated and that an alkyne has been formally reduced to an alkenyl. This alkenyl C=C bond length is also longer than the other, formally a C≡C triple bond (1.407(7) and 1.363(7) Å, respectively), although both are elongated as expected.

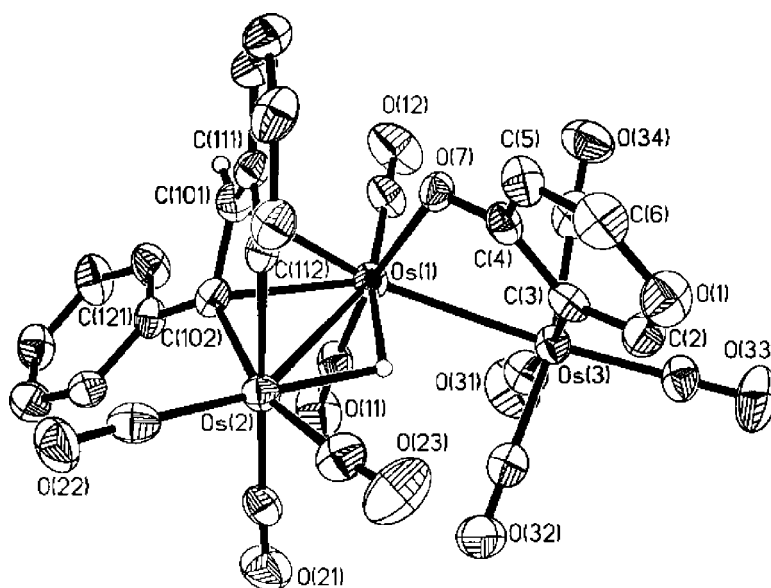


Fig. 2. ORTEP diagram (50% probability thermal ellipsoids; aromatic and pyrone hydrogens omitted) and selected bond lengths (Å) and angles (°) of **3a**. $\text{Os}(1)-\text{Os}(2)=2.9809(4)$; $\text{Os}(1)-\text{Os}(3)=2.8535(4)$; $\text{Os}(1)-\text{O}(7)=2.139(4)$; $\text{Os}(1)-\text{C}(102)=2.330(6)$; $\text{Os}(1)-\text{C}(101)=2.363(6)$; $\text{Os}(2)-\text{C}(102)=2.118(6)$; $\text{Os}(2)-\text{C}(112)=2.129(6)$; $\text{Os}(3)-\text{C}(3)=2.129(6)$; $\text{O}(1)-\text{C}(6)=1.351(8)$; $\text{O}(1)-\text{C}(2)=1.355(8)$; $\text{O}(7)-\text{C}(4)=1.260(7)$; $\text{C}(2)-\text{C}(3)=1.361(8)$; $\text{C}(3)-\text{C}(4)=1.466(9)$; $\text{C}(4)-\text{C}(5)=1.424(8)$; $\text{C}(5)-\text{C}(6)=1.319(9)$; $\text{C}(101)-\text{C}(102)=1.393(9)$; $\text{C}(101)-\text{C}(111)=1.480(8)$; $\text{C}(102)-\text{C}(121)=1.513(8)$; $\text{Os}(3)-\text{Os}(1)-\text{Os}(2)=111.707(10)$; $\text{O}(7)-\text{Os}(1)-\text{Os}(3)=80.61(10)$; $\text{C}(3)-\text{Os}(3)-\text{Os}(1)=81.20(17)$.

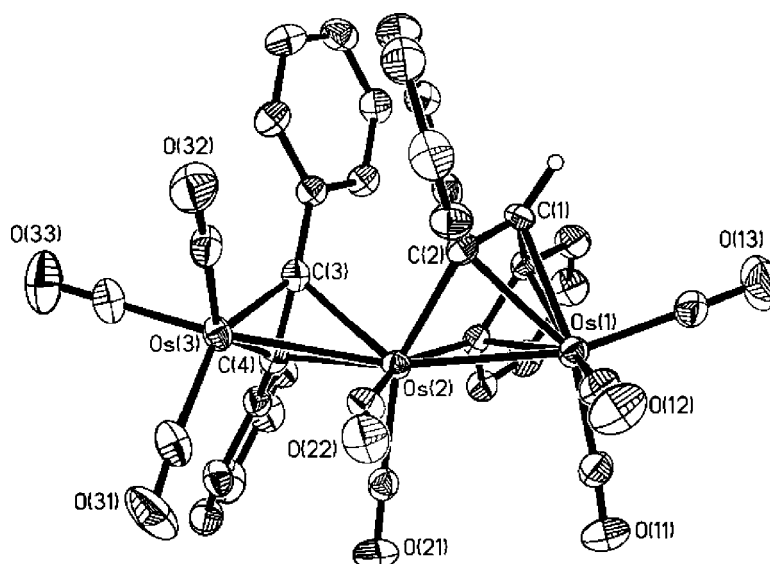
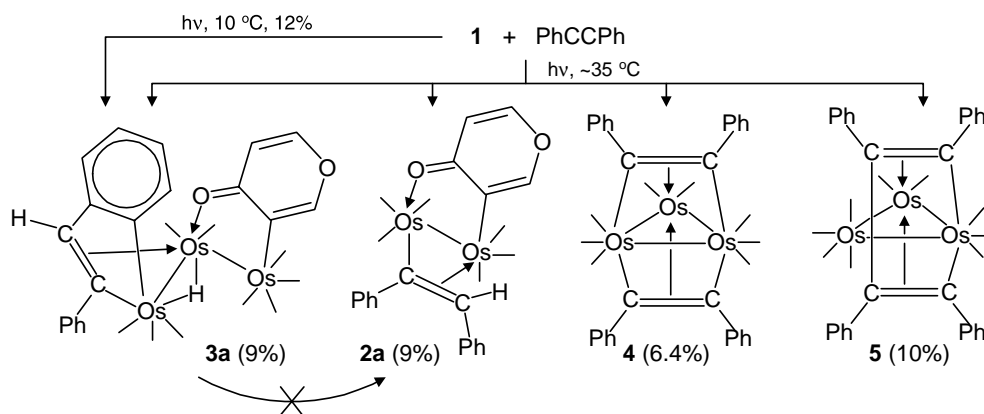
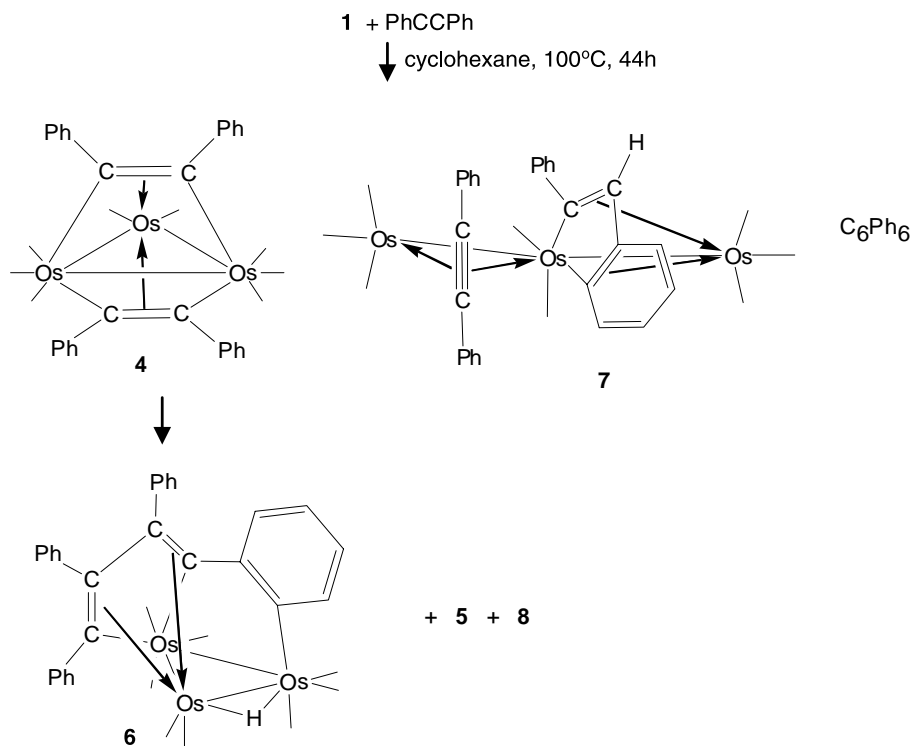


Fig. 3. ORTEP diagram (50% probability thermal ellipsoids; aromatic hydrogens omitted) and selected bond lengths (Å) and angles (°) of **7**. Os(1)–Os(2) = 2.7298(3); Os(2)–Os(3) = 2.7985(3); Os(1)–C(1) = 2.252(4); Os(1)–C(2) = 2.328(5); Os(1)–C(101) = 2.303(5); Os(1)–C(102) = 2.334(5); Os(2)–C(102) = 2.095(5); Os(2)–C(2) = 2.107(5); Os(2)–C(3) = 2.232(5); Os(2)–C(4) = 2.259(5); Os(3)–C(3) = 2.066(5); Os(3)–C(4) = 2.078(5); C(1)–C(2) = 1.407(7); C(3)–C(4) = 1.363(7); C(1)–C(101) = 1.440(7); C(2)–C(201) = 1.487(6); C(3)–C(301) = 1.484(6); C(4)–C(401) = 1.476(7); Os(1)–Os(2)–Os(3) = 155.056(9); C(4)–C(3)–C(301) = 140.3(4); C(3)–C(4)–C(401) = 140.2(4).

Clusters **4**, **6** and **7** are isomers. A comparison of the reported structure of **4** [6], with those of **6** and **7** here show that the essential structural differences among these three clusters are: (i) both **4** and **6** contain a triangular Os₃ framework while **7** comprises a triosmium chain, (ii) orthometallation of a phenyl ring of an alkyne has occurred in **6** and **7** but not in **5**, and (iii) there is no coupling of the two alkynes in **4** and **7**, while in **6** a C–C bond has been formed between the two alkynes.

We have monitored the reaction between **1** and PhCCPh at 130 °C in d₈-toluene (in a Carius) via ¹H NMR spectroscopy, and found that compound **6** was formed after a few hours but was slowly consumed; **5** was also detected although not isolated. Heating a sample of **4** at 100 °C for 4 h resulted in the formation of

5 and **6** (by IR and ¹H NMR spectroscopy), while heating a sample of **7** in d₈-toluene (in a Carius) at 100 °C showed that it was converted completely to another unidentified compound (ν_{CO} 2078m, 2045s, 2015vs, 2002s, 1990w, 1983w, 1971w, 1967w, 1957vw cm⁻¹) after 40 h. We have also carried out the reaction between Os₃(CO)₁₀(NCCH₃)₂ and PhCCPh at room temperature, which gave only **4** and **5** but no **7**. Thus these results show that **4** is the precursor to **5** (the formation of **5**, and **8**, from **4** have been reported [7,18]) and **6** but not to **7**, and that the formation of **7** may be activated by the γ -pyrone ligand. However, we have also found that the reaction of **3a** with excess PhCCPh at 110 °C did not give **7**, indicating that **3a** is not a precursor to **7** in the thermal reaction of **1** with PhCCPh. The results also



Scheme 2.

indicate that **2a** does not arise from the photochemical or thermal decomposition of **3a**. This is also corroborated by the different products obtained here compared to the case for $\text{Os}_3(\text{CO})_{12}$ [6,9]. Thus the reaction pathway for **1** with PhCCPh is as depicted in Scheme 2.

2.2. Reactions with other alkynes

Similar reactions were also carried out with a number of other alkynes. Thus the photolysis of **1** with $t\text{BuCCH}$, $t\text{BuCCMe}$ and EtCCEt gave the corresponding dinuclear complexes $\text{Os}_2(\text{CO})_6(\mu-\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu\text{-L})$ (where $\text{L} = t\text{BuCHCH}$ (**2b**), $t\text{BuCHCMe}$ (**2c**) or EtCHCEt (**2d**)) in good yields. These reactions yet again contrast with those of $\text{Os}_3(\text{CO})_{12}$ [10]. There are minor differences in behaviour with each alkyne; for instance, EtCCEt gave the same product (**2d**) using the thermal route, while the photochemical reaction with PhCCH afforded only the trinuclear species $\text{Os}_3(\text{CO})_9(\mu\text{-H})(\mu-\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu\text{-HCCHC}_6\text{H}_4)$ (**3b**) and the thermal reaction (at 100°C) did not proceed. The clusters have all been characterised spectroscopically and analytically, and in the case of **2b**, **2d** and **3b**, also by single crystal X-ray crystallography.

The structures of **2a** and **2d** are similar, while **2b** has a different orientation of the alkyne substituents relative to the pyrone; the ORTEP diagram of **2b** is shown in Fig. 4. Thus the alkyne is twisted such that the substituent on the μ_2 alkyne carbon (C(31)) in **2a** or **2d** is pointing away from the pyrone, while the H atom on that carbon in **2b** is pointing towards the pyrone. A

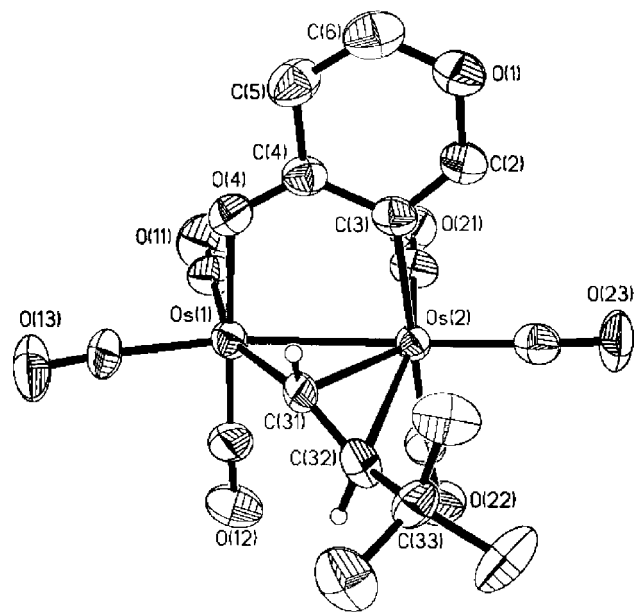
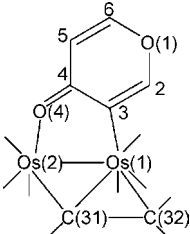


Fig. 4. ORTEP diagram of **2b** (50% probability thermal ellipsoids; methyl and pyrone hydrogens omitted).

common atomic numbering scheme and selected bond parameters for clusters **2** are given in Table 1.

The Os–Os bond lengths in these complexes are rather short, although this appears to be a feature common to most of the relatively small number of osmium complexes reported [11]. The variations in C–O and C–C bond distances for the γ -pyrone are consistent with

Table 1
Common cluster numbering scheme and selected bond lengths (Å) and bond angles (°) for **2a**, **2b** and **2d**



	2a	2b	2d
Bond length (Å)			
Os(1)–Os(2)	2.76411(19)	2.7723(6)	2.7732(3)
Os(1)–C(3)	2.167(3)	2.163(12)	2.152(5)
Os(2)–O(4)	2.112(2)	2.111(8)	2.132(4)
Os(1)–C(31)	2.358(3)	2.286(10)	2.327(5)
Os(1)–C(32)	2.343(3)	2.423(12)	2.333(4)
Os(2)–C(31)	2.112(3)	2.087(11)	2.229(5)
O(1)–C(6)	1.340(4)	1.310(17)	1.314(7)
O(1)–C(2)	1.366(4)	1.347(15)	1.348(7)
O(4)–C(4)	1.272(4)	1.285(13)	1.283(7)
C(2)–C(3)	1.347(4)	1.326(17)	1.355(7)
C(3)–C(4)	1.445(4)	1.423(17)	1.447(7)
C(4)–C(5)	1.426(5)	1.434(17)	1.412(8)
C(5)–C(6)	1.335(5)	1.339(19)	1.350(9)
C(31)–C(32)	1.393(5)	1.309(17)	1.368(7)
Bond angle (°)			
O(4)–Os(2)–Os(1)	85.16(6)	86.1(2)	84.88(10)
C(3)–Os(1)–Os(2)	82.98(8)	83.7(3)	83.39(14)

retention of the pyrone character of that ligand, while the C(31)–C(32) distances (1.309(17)–1.393(5) Å) suggest that the alkyne bond order has been reduced to somewhere between that of a C–C single and a C=C double bond [12]. As has already been observed for **1** [3], the carbonyl ligand *trans* to the O-donor atom of the pyrone is closer to the Os, consistent with an increase in π -back bonding into the carbonyl; this is also true for clusters **3**.

Clusters **3a** and **3b** have a bent triosmium chain, and like **2**, they also differ in the relative orientation of the alkyne and pyrone ligands; the ORTEP diagram of **3b**, together with selected bond parameters, is given in Fig. 5.

As can be clearly discerned, a phenyl ring of the alkynes is orthometallated; in **3a**, the orthometallated ring is on the same side of the triosmium plane as the pyrone, while in **3b**, it is on the opposite side. As may be expected, this imposes steric strains in **3a**, which is manifested in the twisting of the pyrone ring w.r.t the Os–Os bond which it bridges; the torsion angle between the pyrone and this Os–Os edge (C(4)C(3)Os(3)Os(1)) is 26.5° compared to 12.2° (for C(4)C(3)Os(3)Os(2)) in **3b**. Interestingly, the two C(alkyne) to central Os bond lengths are very different for **3b** (2.220(6) and 2.457(7) Å), while that for **3a** are more equal.

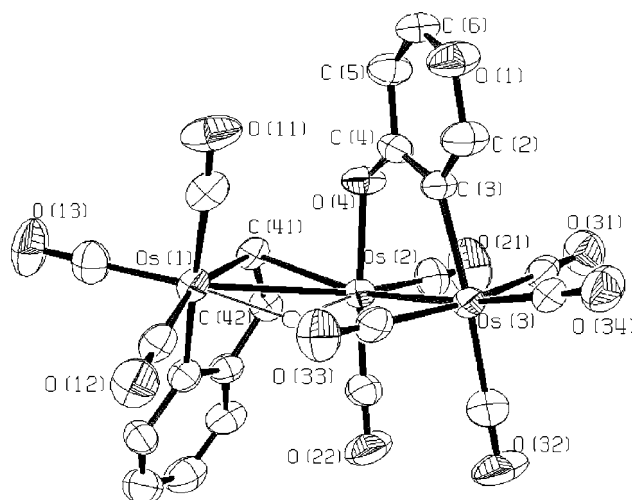


Fig. 5. ORTEP diagram (50% probability thermal ellipsoids; aromatic and pyrone hydrogens omitted) and selected bond lengths (Å) and angles (°) of **3b**. Os(1)–Os(2) = 2.9855(4); Os(2)–Os(3) = 2.8805(4); Os(1)–C(41) = 2.113(6); Os(1)–C(44) = 2.140(8); Os(2)–O(4) = 2.144(5); Os(2)–C(41) = 2.220(6); Os(2)–C(42) = 2.457(7); Os(3)–C(3) = 2.141(7); O(1)–C(6) = 1.330(9); O(1)–C(2) = 1.362(10); O(4)–C(4) = 1.274(9); C(2)–C(3) = 1.364(10); C(3)–C(4) = 1.429(10); C(4)–C(5) = 1.428(10); C(5)–C(6) = 1.315(11); Os(3)–Os(2)–Os(1) = 109.914(11); O(4)–Os(2)–Os(3) = 83.48(14); C(3)–Os(3)–Os(2) = 82.8(2).

As **1** is stable both photochemically and thermally, it would appear that formation of the dinuclear compounds **2** occurs via fragmentation of a trinuclear cluster in which the alkyne has already been incorporated. That such an intermediate species is plausible is exemplified by the reaction with ^tBuCCMe, for which the trinuclear cluster Os₃(CO)₈(μ-CO)(μ-γ-C₅H₃O₂)(^tBuCHCHCH₂) (**9**) was also isolated from the photochemical reaction, in 8% yield. From the same reaction was also isolated a trace amount of Os₃(CO)₁₂, and two unidentified complexes **A** and **B**; the latter decomposed during attempts at TLC separation. Similar products were obtained when the irradiation was carried out with UV light.

The spectroscopic data assignable to **A** suggests that it is a carbonyl cluster containing γ-pyrone and an allyl group. The carbonyl ligands are indicated in the IR spectrum; the γ-pyrone is indicated in the ¹H resonances comprising of a singlet and two doublets at δ 7.99 ppm (1H), 7.67 ppm (1H) and 6.06 ppm (1H), corresponding to H₂, H₆ and H₅, respectively, and the allyl group by three doublets and a doublet of triplets at δ 6.06 ppm (1H), 3.53 ppm (1H), 2.96 ppm (1H) and 4.71 ppm (1H), corresponding to the allylic hydrogens ^tBuCHCHCH₂, ^tBuCHCHCHH, ^tBuCHCHCHH and ^tBuCHCHCH₂, respectively, as well as a singlet at δ 1.15 ppm (9H) for the *t*-butyl group.

The structure of **9** has been characterised by an X-ray crystallographic study; the ORTEP diagram is presented in Fig. 6, together with selected bond parameters.

Cluster **9** contains an allyl ligand, presumably formed via migration of the metal hydride onto the alkyne;

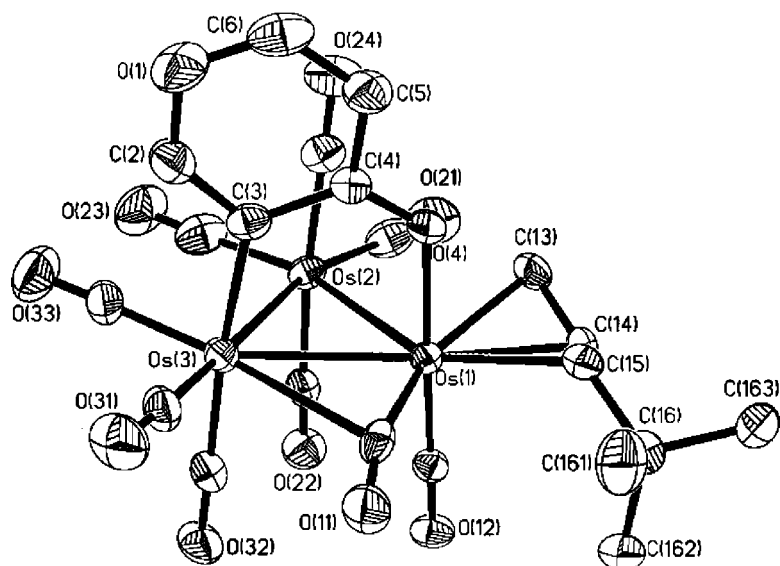


Fig. 6. ORTEP diagram (50% probability thermal ellipsoids; aromatic hydrogens omitted) and selected bond lengths (Å) and angles (°) of **9**. Os(1)–Os(2) = 2.8863(4); Os(1)–Os(3) = 2.8543(4); Os(2)–Os(3) = 2.8559(4); Os(1)–C(12) = 1.854(7); Os(1)–C(11) = 1.893(7); Os(1)–O(4) = 2.124(5); Os(1)–C(13) = 2.248(7); Os(1)–C(14) = 2.260(7); Os(1)–C(15) = 2.312(7); Os(3)–C(3) = 2.129(7); Os(3)–C(11) = 2.605(7); O(1)–C(6) = 1.326(10); O(1)–C(2) = 1.368(9); O(4)–C(4) = 1.262(8); C(13)–C(14) = 1.385(9); C(14)–C(15) = 1.394(10); C(15)–C(16) = 1.543(10); C(2)–C(3) = 1.355(10); C(3)–C(4) = 1.440(10); C(4)–C(5) = 1.437(9); C(5)–C(6) = 1.353(11); Os(3)–Os(1)–Os(2) = 59.666(9); Os(3)–Os(2)–Os(1) = 59.610(9); Os(1)–Os(3)–Os(2) = 60.723(9); O(4)–Os(1)–Os(3) = 83.93(13); C(3)–Os(3)–Os(1) = 83.0(2).

carrying out the photochemical reaction in the presence of H_2 gave a similar yield of **9**. Although allyl-substituted triosmium clusters are well documented, those with the allyl ligand coordinated to only one osmium centre are rare; the only examples reported so far are the linear clusters $\text{Os}_3\text{Br}(\text{CO})_{10}(\text{NCR})(\eta^3\text{-C}_3\text{H}_5)$ ($\text{R} = \text{Pr}$, PhCH_2CH_2) [13], and the cationic, triangular cluster $[\text{Os}_3(\text{CO})_{11}(\eta^3\text{-C}_3\text{H}_5)]^+\text{BF}_4^-$ [14]. Another striking feature of **9** is the presence of a semi-bridging carbonyl (Os(1)–C(11) = 1.893(7) Å and Os(3)–C(11) = 2.605(7) Å), an uncommon feature among osmium clusters. Semi-bridging carbonyl groups are better π -acceptors than terminal carbonyls [15]; the strongly electron donating allyl group may be responsible for the adoption of a semi-bridging carbonyl in **9**.

That **9** is formed only photochemically and not thermally is corroborated by the observation that the reaction between **1** and $t\text{-BuCCMe}$ carried out at 110 °C for 16 h resulted in the formation of **2c** (56%), a trace amount of $\text{Os}_3(\text{CO})_{12}$, and a low yield of another unidentified product **C**. Although the structure of **C** has not been determined, its IR spectroscopic data suggests a cluster compound. Its ^1H NMR spectrum contains three doublets and a doublet of triplets at δ 3.78 ppm (1H), 3.70 ppm (1H), 2.23 ppm (1H) and 5.17 ppm (1H), assignable to the allylic hydrogens $t\text{-BuCHCHCH}_2$, $t\text{-BuCHCHCHH}$, $t\text{-BuCHCHCHH}$ and $t\text{-BuCHCHCH}_2$, respectively, and a singlet at δ 1.23 ppm (9H) assignable to the t -butyl group. These resonances, together with the absence of any resonances assignable to a pyrone, suggest that it is an alkyne carbonyl cluster. Monitoring by

^1H NMR of the irradiation of a CDCl_3 solution of **9** showed that unknown **B** was formed, but not **A**, **C** nor **2c**, thus ruling out cluster **9** as a precursor to **A**, **C** or **2c**.

3. Conclusion

The reactions of cluster **1** with various alkynes show a tendency towards metal–metal bond scission. Photochemical activation appears to lead generally to retention of the pyrone ligand with metal–metal bond scission, resulting in the formation of dinuclear or trinuclear chain products. On the other hand, the thermal reactions are more varied, ranging from no reaction to affording similar dinuclear products as the photochemical reaction. In the case of PhCCPh , however, cleavage of the γ -pyrone from the cluster is favoured. Furthermore, we have not observed any change in bonding mode of, or reaction directly involving, the pyrone. These are in contrast to the reactivities observed for the clusters containing N-donor bridging ligands, such as the imidoyl or iminium systems.

4. Experimental

4.1. General procedures

All reactions and manipulations were carried out under nitrogen by using standard Schlenk techniques. Solvents were purified, dried, distilled and stored under

nitrogen prior to use. IR spectra were recorded as hexane solutions unless otherwise stated. NMR spectra were recorded on a Bruker ACF-300 FT-NMR spectrometer as CDCl_3 solutions unless otherwise stated. ^1H chemical shifts reported are referenced against the residual proton signals of the solvents. ESI spectra were obtained on a Finnigan MAT LCQ, with a spray voltage of 4.5 kV and capillary temperature of 353 K, as CH_3CN solutions. FAB mass spectra were recorded on a Finnigan MAT 95XL-T Mass Spectrometer in an *m*-nitrobenzyl alcohol matrix. EI spectra were obtained on a Macromass VG7035, at 70 eV. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore. The preparation of $\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\gamma\text{-C}_5\text{H}_3\text{O}_2)$ (**1**) has been described previously [3]. The cluster $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ was prepared according to a literature method [16]. All other reagents were from commercial sources and used as supplied. TLC separations were on silica plates of 0.25 or 0.5 mm thickness and extracted with dichloromethane. In photochemical reactions, irradiation with visible light was performed with an OSRAM or a Tungsraflex 60 W lamp. NMR-scale experiments were carried out in an NMR tube fitted with a Teflon valve, purchased from Kontes.

4.2. Photochemical reactions of **1**

4.2.1. With $\text{PhC}\equiv\text{CPh}$

A solution of **1** (22.0 mg, 0.023 mmol) and $\text{PhC}\equiv\text{CPh}$ (42.0 mg, 0.24 mmol) in cyclohexane (16 ml) was placed in a Carius tube, degassed by three freeze–pump–thaw cycles and irradiated with visible light at 35 °C for 2 d. The solvent was removed under reduced pressure and the residue chromatographed on silica TLC plates. Elution with hexane/ CH_2Cl_2 (4/1, v/v) gave four major bands.

Band 1 ($R_f = 0.54$) gave red crystalline samples of the known cluster $\text{Os}_3(\text{CO})_8(\text{PhCCPh})_2$ (**4**) (1.7 mg, 6.4 mmol) as identified by its IR spectrum [6].

Band 2 ($R_f = 0.46$) gave purple crystalline samples of $\text{Os}_3(\text{CO})_9(\text{PhCCPh})_2$ (**5**) (2.7 mg, 10%): IR ν_{CO} 2114m, 2058vs, 2043s, 2036m(sh), 2012s, 1999m, 1988w(sh), 1974m, 1930m (lit.: [7] 2113m, 2057vs, 2042s, 2037sh, 2011s, 1998m, 1990sh, 1972m).

Band 3 ($R_f = 0.27$) gave pale yellow crystalline $\text{Os}_2(\text{CO})_6(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu\text{-PhCCHPh})$ (**2a**) (5.7 mg, 30%): IR ν_{CO} 2079m, 2062vw, 2047s, 2000s, 2000s, 1990m(sh), 1972m, 1964w(sh); ^1H NMR δ 8.17 (1H, s, H2), 7.83 (1H, d, $^3J_{56} = 5.0$ Hz, H6), 7.3–6.9 (10H, m, phenyl), 6.33 (1H, d, H5), 4.15 (1H, s, =CH). Calc. for $\text{C}_{25}\text{H}_{14}\text{O}_8\text{Os}_2$: C, 36.49; H, 1.71. Found: C, 36.81; H, 1.63%.

Band 4 ($R_f = 0.16$) gave yellow crystalline $\text{Os}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu\text{-PhCCHC}_6\text{H}_4)$ (**3a**) (2.2 mg, 9%): IR ν_{CO} 2111m, 2078m, 2044m, 2034vs, 2020m, 2005s, 1996m(sh), 1960w; ^1H NMR δ 7.67 (1H, s, H3), 7.64 (1H, d, $^3J_{56} = 5.4$ Hz, H5), 7.81 (2H, d, H2' and

H6'), 7.35 (2H, t, H3' and H5'), 7.25 (1H, d, H3''), 7.19 (1H, t, H4'), 7.00 (1H, d, H6''), 6.84 (1H, t, H5''), 6.74 (1H, t, H4''), 4.99 (1H, d, H6), 4.15 (1H, s, =CH), –13.3 (1H, s, OsHOs). Calc. for $\text{C}_{28}\text{H}_{14}\text{O}_{11}\text{Os}_3$: C, 30.65; H, 1.29. Found: C, 30.59; H, 1.28%.

A similar reaction of **1** (21.8 mg, 0.023 mmol) with $\text{PhC}\equiv\text{CPh}$ (20.5 mg, 0.11 mmol) in cyclohexane at 10 °C for 44 h gave unreacted **1** (1.9 mg) and **3a** (3.0 mg, 12%).

4.2.2. With $^t\text{BuC}\equiv\text{CH}$

A similar reaction of **1** (42.6 mg, 0.045 mmol) with $^t\text{BuC}\equiv\text{CH}$ (5 drops) in CH_2Cl_2 (5 ml) for 3 d, followed by a similar work up, gave colourless crystals of $\text{Os}_2(\text{CO})_6(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu\text{-}^t\text{BuCHCH})$ (**2b**) ($R_f = 0.35$, yield 20.0 mg, 61%). IR ν_{CO} 2081m, 2046s, 2003vs, 1986w, 1971w, 1965m(sh); ^1H NMR δ 7.85 (1H, s, H2), 7.71 (1H, d, $^3J_{56} = 5.2$ Hz, H6), 6.42 (1H, d, H5), 4.97 (1H, d, $^3J_{\text{HH}} = 15$ Hz, $^t\text{BuCHCH}$), 3.33 (1H, d, $^t\text{BuCHCH}$), 1.09 (9H, s, ^tBu). Calc. for $\text{C}_{17}\text{H}_{14}\text{O}_8\text{Os}_3$: C, 28.10; H, 1.94. Found: C, 28.19; H, 2.02%.

4.2.3. With $\text{PhC}\equiv\text{CH}$

A similar reaction of **1** (46.4 mg, 0.049 mmol) with $\text{PhC}\equiv\text{CH}$ (8 drops) in hexane (25 ml) for 3 d gave, after work up, unreacted **1** ($R_f = 0.45$, 27.0 mg) and yellow $\text{Os}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu\text{-HCCHC}_6\text{H}_4)$ (**3b**) ($R_f = 0.24$, yield 2.6 mg, 5.2%). IR ν_{CO} 2121m, 2077m, 2047m, 2035vs, 2018m, 2003s, 1993m(sh), 1958m; ^1H NMR δ 7.95 (1H, s, H2), 7.77 (1H, d, $^3J_{56} = 5.4$ Hz, H6), 6.7–6.9 (4H, m, aromatic), 6.26 (1H, d, H5), 4.07 (1H, s, =CH), –12.4 (1H, s, OsHOs). Calc. for $\text{C}_{22}\text{H}_{10}\text{O}_{11}\text{Os}_3$: C, 25.88; H, 0.99. Found: C, 26.12; H, 0.88%.

4.2.4. With $^t\text{BuC}\equiv\text{CMe}$

A similar reaction of **1** (38.6 mg, 0.041 mmol) with $^t\text{BuC}\equiv\text{CMe}$ (0.2 ml) in CH_2Cl_2 for 6 h gave, after workup, a trace amount of $\text{Os}_3(\text{CO})_{12}$ (identified by its IR spectrum), an unstable compound **B** which decomposed during the TLC separation (as judged spectroscopically), and the following three bands:

Band 1 ($R_f = 0.60$) gave red crystalline $\text{Os}_3(\text{CO})_8(\mu\text{-CO})(\mu\text{-}\gamma\text{-C}_5\text{H}_3\text{O}_2)(^t\text{BuCHCHCH}_2)$ (**9**) (3.3 mg, 8.0%): IR ν_{CO} 2093m, 2047vs, 2017vs, 2002s, 1991m, 1984m(sh), 1967w; ^1H NMR δ 7.93 (1H, s, H2), 7.62 (1H, d, $^3J_{56} = 5.0$ Hz, H6), 6.11 (1H, d, H5), 5.10 (1H, d, $^3J_{\text{HH}} = 7.4$ Hz, $^t\text{BuCHCHCH}_2$), 4.86 (1H, dt, $^3J_{\text{HH}} = 12$ Hz, $^t\text{BuCHCHCH}_2$), 3.56 (2H, d, $^t\text{BuCHCHCH}_2$), 1.34 (9H, s, ^tBu). FAB-MS m/z 1015.9 $[\text{M}]^+$. Exact mass fragments at 1014.943, 1015.947 and 1016.947 matched $\text{C}_{21}\text{H}_{16}\text{O}_{11}\text{Os}_3$.

Band 2 ($R_f = 0.52$) gave a yellow compound **A**, which could not be completely separated from **2c**. IR ν_{CO} 2095m, 2077w, 2023w, 2014s, 1992s, 1982m, 1966w, 1928m; ^1H NMR δ 7.99 (1H, s, H2), 7.67 (1H, d, $^3J_{56} = 5.8$ Hz, H6), 6.06 (1H, d, H5), 4.72 (1H, dt, $^3J_{\text{HH}} = 7.4$, 12 Hz, $^t\text{BuCHCHCH}_2$), 3.53 (1H, d, $^t\text{BuCHCHCH}_2$), 2.96 (2H, d, $^t\text{BuCHCHCH}_2$), 1.15 (9H, s, ^tBu).

Band 3 ($R_f = 0.49$) light yellow $\text{Os}_2(\text{CO})_6(\mu-\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu\text{-}^t\text{BuCHCMe})$ (**2c**) (16.6 mg, 55%): IR ν_{CO} 2077m, 2043s, 1998s, 1989w(sh), 1982m, 1974m, 1966m; $^1\text{H NMR}$ δ 8.11 (1H, s, H2), 7.77 (1H, d, $^3J_{56} = 5.0$ Hz, H6), 6.18 (1H, d, H5), 3.38 (3H, s, Me), 2.97 (1H, s, $^t\text{BuCH}$), 1.15 (9H, s, ^tBu). FAB-MS m/z 742 $[\text{M}]^+$, 713 $[\text{M} - \text{CO}]^+$, 686 $[\text{M} - 2\text{CO}]^+$, 656 $[\text{M} - 3\text{CO}]^+$, 627 $[\text{M} - 4\text{CO}]^+$, 600, $[\text{M} - 5\text{CO}]^+$.

4.3. Thermal reactions of **1**

4.3.1. With $\text{PhC}\equiv\text{CPh}$

A solution of **1** (29.5 mg, 0.031 mmol) and $\text{PhC}\equiv\text{CPh}$ (11.1 mg, 0.062 mmol) in cyclohexane (10 ml) was placed in a Carius tube and degassed by three freeze–pump–thaw cycles. After being heated at 100 °C for 44 h, the solvent was removed under reduced pressure and the residue re-dissolved in the minimum volume of dichloromethane for chromatographic separation on TLC plates to afford five bands.

Band 1 ($R_f = 0.68$) gave red crystalline **4** (yield 3.8 mg, 11%) which was identified spectroscopically [6].

Band 2 ($R_f = 0.58$) gave red crystalline samples of the previously reported compound $\text{Os}_3(\text{CO})_8(\mu\text{-H})(\mu\text{-PhCCPhCPhCC}_6\text{H}_4)$ (**6**) (6.5 mg, 18%): IR ν_{CO} 2095m, 2057m, 2033s, 2019w, 2011w(sh), 1996w, 1988vw(sh), 1976w. (Lit.: [7] (CCl_4) 2096s, 2058s, 2033vs, 2020m, 2012m, 1997m, 1990sh, 1977m); $^1\text{H NMR}$ δ 7.9–5.8 (16H, m, aromatic), –14.9 (1H, s, OsHOs).

Band 3 ($R_f = 0.36$) gave unreacted **1** (9.1 mg), identified spectroscopically.

Band 4 ($R_f = 0.22$) gave red crystalline $\text{Os}_3(\text{CO})_8(\mu\text{-PhCCPh})(\mu\text{-PhCCHC}_6\text{H}_4)$ (**7**) (13.2 mg, 37%): IR ν_{CO} 2087s, 2056vs, 2025s, 2013s, 2002w, 2000w, 1977s, 1968m(sh); (CH_2Cl_2): 2089s, 2052s, 2025m, 2015m(sh), 1996w(sh), 1965m(br), 1908vw(br); $^1\text{H NMR}$ δ (CD_2Cl_2): 7.7–6.5 (m, aromatic). Calc. for $\text{C}_{36}\text{H}_{20}\text{-O}_8\text{Os}_3$: C, 37.56; H, 1.75. Found: C, 37.32; H, 2.02%.

Band 5 ($R_f \approx 0$) gave colourless crystals of hexaphenylbenzene, identified by $^1\text{H NMR}$ and EI-MS [17].

A second set of the same reaction under similar conditions afforded, in addition to the above, also trace amounts of **5** and the previously reported compound $\text{Os}_3(\text{CO})_7(\text{PhCCPh})_3$ (**8**) [18], both identified spectroscopically.

4.3.2. With $\text{EtC}\equiv\text{CEt}$

A solution of **1** (14.9 mg, 0.016 mmol) and $\text{EtC}\equiv\text{CEt}$ (0.05 ml) in CDCl_3 was prepared in an NMR tube fitted with a Teflon valve and degassed by three freeze–pump–thaw cycles. This was then heated at 110 °C for 16 h. TLC separation with hexane/ CH_2Cl_2 (4/1, v/v) as the mobile phase afforded one major band ($R_f = 0.50$) from which light yellow crystalline $\text{Os}_2(\text{CO})_6(\mu-\gamma\text{-C}_5\text{H}_3\text{O}_2)(\mu\text{-EtCCHEt})$ (**2d**) (10.0 mg, 85%) was obtained: IR ν_{CO} 2078m, 2044s, 1998s, 1989w(sh), 1983m, 1975m, 1967m,

1960w(sh); $^1\text{H NMR}$ δ 8.12 (1H, s, H2), 7.78 (1H, d, $^3J_{56} = 5.0$ Hz, H6), 6.18 (1H, d, H5), 3.1 (2H, m, CH_2), 2.84 (1H, m, CH), 2.5 (1H, m, CHH), 2.1 (1H, m, CHH), 1.40 (3H, t, $^3J_{\text{HH}} = 7.4$ Hz, CH_3), 1.02 (3H, t, CH_3). FAB-MS (m/z) 728 $[\text{M}]^+$, 698 $[\text{M} - \text{CO}]^+$, 670 $[\text{M} - 2\text{CO}]^+$, 644 $[\text{M} - 3\text{CO}]^+$, 614 $[\text{M} - 4\text{CO}]^+$, 584 $[\text{M} - 5\text{CO}]^+$, 556 $[\text{M} - 6\text{CO}]^+$. Calc. for $\text{C}_{17}\text{H}_{14}\text{O}_8\text{Os}_2$: C, 28.10; H, 1.94. Found: C, 28.85; H, 2.08%.

4.3.3. With $^t\text{BuC}\equiv\text{CMe}$

A similar reaction of **1** (27.3 mg, 0.029 mmol) and $\text{EtC}\equiv\text{CEt}$ (0.05 mL) gave, after workup as above, a trace amount of $\text{Os}_3(\text{CO})_{12}$ (**2c**) (12.0 mg, 56%), and an unidentified yellow compound **C** ($R_f = 0.05$, yield 1.1 mg): IR ν_{CO} 2099m, 20772s, 2062m, 2051m, 2043w, 2026s, 2004s, 1988s, 1972w(sh); $^1\text{H NMR}$ δ 5.17 (1H, dt, $^3J_{\text{HH}} = 7.0$, 12 Hz, $^t\text{BuCHCHCH}_2$), 3.78 (1H, d, $^3J_{\text{HH}} = 6.6$ Hz, $^t\text{BuCHCHCH}_2$), 3.70 (1H, d, $^t\text{BuCHCHCHH}$), 2.23 (1H, d, $^t\text{BuCHCHCHH}$), 1.23 (9H, s, ^tBu).

4.4. Reaction of $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ with $\text{PhC}\equiv\text{CPh}$

A solution of $\text{Os}_3(\text{CO})_{10}(\text{NCCH}_3)_2$ (32.4 mg, 0.035 mmol) and $\text{PhC}\equiv\text{CPh}$ (6.2 mg, 0.035 mmol) in CH_2Cl_2 (15 ml) was degassed in a Carius tube by three freeze–pump–thaw cycles and then stirred at RT for 13 h. Chromatographic separation by TLC with hexane/ CH_2Cl_2 (4/1, v/v) as the mobile phase gave yellow **4** ($R_f = 0.52$, yield 1.6 mg, 4.0%) [6] and dark purple crystalline **5** ($R_f = 0.47$, yield 13.3 mg, 32%) [7], both identified by their IR spectra.

4.5. Crystal structure determinations

Crystals were grown from dichloromethane (or dibromomethane)/hexane solutions and mounted on quartz fibres. X-ray data were collected on a Bruker AXS APEX system, using Mo $\text{K}\alpha$ radiation, with the SMART suite of programs [19]. Data were processed and corrected for Lorentz and polarisation effects with SAINT [20], and for absorption effects with SADABS [21]. Structural solution and refinement were carried out with the SHELXTL suite of programs [22]. Crystal and refinement data are summarised in Tables 2 and 3.

The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. Organic hydrogens were placed in calculated positions, except for **2a** and **3a** in which the H on the alkyne was located in the difference map. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model (but see below). Metal hydrides were placed in positions calculated with XHYDEX [23] and refined with a fixed isotropic thermal parameter and riding on one of the osmium atoms it is attached to.

Table 2
Crystal data for clusters **2a**, **2b**, **2d**, **3a** and **3b**

Compound code	2a	2b	2d	3a	3b
Empirical formula	C ₂₅ H ₁₄ O ₈ Os ₂	C ₁₇ H ₁₄ O ₈ Os ₂	C ₁₇ H ₁₄ O ₈ Os ₂	C ₂₈ H ₁₄ O ₁₁ Os ₃	C ₂₂ H ₁₀ O ₁₁ Os ₃
Formula weight	822.76	726.68	726.68	1096.99	1020.90
Temperature (K)	173(2)	223(2)	223(2)	223(2)	223(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.2401(4)	9.2600(14)	9.4835(2)	9.5336(4)	8.9921(2)
<i>b</i> (Å)	10.3457(4)	13.5435(19)	9.5843(2)	32.3465(15)	10.8710(3)
<i>c</i> (Å)	11.6577(5)	15.333(2)	10.9083(2)	9.0914(4)	12.8541(3)
α (°)	98.747(1)	90	80.941(1)	90	102.237(1)
β (°)	94.815(1)	95.696(3)	78.699(1)	101.575(1)	100.493(1)
γ (°)	108.529(1)	90	87.297(1)	90	97.515(1)
Volume (Å ³)	1145.80(8)	1913.4(5)	960.00(3)	2746.6(2)	1188.54(5)
<i>Z</i>	2	4	2	4	2
Density (calculated) (mg/m ³)	2.385	2.523	2.514	2.653	2.853
Absorption coefficient (mm ⁻¹)	11.129	13.309	13.263	13.907	16.056
<i>F</i> (000)	760	1328	664	1992	916
Crystal size (mm ³)	0.32 × 0.18 × 0.16	0.04 × 0.16 × 0.28	0.32 × 0.28 × 0.15	0.12 × 0.16 × 0.17	0.18 × 0.26 × 0.28
Theta range for data collection (°)	2.11 to 31.46	2.01 to 25.03	1.93 to 29.34	2.18 to 30.50	2.23 to 29.97
Reflections collected	18320	13023	7832	22502	10886
Independent reflections	7023	3377	4650	8122	6585
	[<i>R</i> _{int} = 0.0366]	[<i>R</i> _{int} = 0.0724]	[<i>R</i> _{int} = 0.0302]	[<i>R</i> _{int} = 0.0519]	[<i>R</i> _{int} = 0.0284]
Completeness (%) (to theta (°))	92.5 (31.46)	100.0 (25.03)	88.6 (29.34)	96.9 (30.50)	95.3 (29.97)
Maximum and minimum transmission	0.267 and 0.148	0.496 and 0.212	0.241 and 0.101	0.266 and 0.175	0.141 and 0.072
Data/restraints/parameters	7023/0/320	3377/0/247	4650/0/246	8122/0/382	6585/0/325
Goodness-of-fit on <i>F</i> ²	0.934	1.015	1.077	0.894	0.955
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0227, <i>wR</i> ₂ = 0.0459	<i>R</i> ₁ = 0.0493, <i>wR</i> ₂ = 0.1224	<i>R</i> ₁ = 0.0276, <i>wR</i> ₂ = 0.0726	<i>R</i> ₁ = 0.0361, <i>wR</i> ₂ = 0.0663	<i>R</i> ₁ = 0.0375, <i>wR</i> ₂ = 0.0794
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0285, <i>wR</i> ₂ = 0.0468	<i>R</i> ₁ = 0.0583, <i>wR</i> ₂ = 0.1276	<i>R</i> ₁ = 0.0311, <i>wR</i> ₂ = 0.0743	<i>R</i> ₁ = 0.0531, <i>wR</i> ₂ = 0.0703	<i>R</i> ₁ = 0.0472, <i>wR</i> ₂ = 0.0821
Largest difference peak and hole (e Å ⁻³)	1.247 and -1.007	4.005 and -2.021	1.992 and -1.945	1.875 and -0.924	1.835 and -2.196

Table 3
Crystal data for clusters **6**, **7** and **9**

Compound code	6	7	9
Empirical formula	C ₃₆ H ₂₀ O ₈ Os ₃ ·CH ₂ Cl ₂	C ₃₆ H ₂₀ O ₈ Os ₃	C ₂₁ H ₁₆ O ₁₁ Os ₃
Formula weight	1236.05	1151.12	1014.94
Temperature (K)	223(2)	193(2)	223(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	<i>a</i> = 17.9706(10)	<i>a</i> = 10.7830(6)	<i>a</i> = 9.0099(2)
<i>b</i> (Å)	<i>b</i> = 8.9568(5)	<i>b</i> = 17.0255(9)	<i>b</i> = 22.1015(5)
<i>c</i> (Å)	<i>c</i> = 23.4649(12)	<i>c</i> = 17.8035(9)	<i>c</i> = 12.8932(3)
β (°)	β = 106.479(1)	β = 100.588(1)	β = 106.773(1)
Volume (Å ³)	3621.7(3)	3212.8(3)	2458.22(10)
<i>Z</i>	4	4	4
Density (calculated) (mg/m ³)	2.267	2.380	2.742
Absorption coefficient (mm ⁻¹)	10.697	11.888	15.525
<i>F</i> (000)	2280	2112	1832
Crystal size (mm ³)	0.40 × 0.30 × 0.28	0.40 × 0.30 × 0.28	0.24 × 0.17 × 0.08
Theta range for data collection (°)	2.36 to 30.57	1.67 to 31.01	2.36 to 30.01
Reflections collected	31182	27361	21065
Independent reflections	10872 [<i>R</i> _{int} = 0.0327]	9817 [<i>R</i> _{int} = 0.0394]	6996 [<i>R</i> _{int} = 0.0725]
Completeness (%) (to theta (°))	97.9 (30.57)	95.8 (31.01)	97.6 (30.01)
Maximum and minimum transmission	0.156 and 0.083	0.124 and 0.059	0.336 and 0.163
Data/restraints/parameters	10,872/16/453	9817/0/424	6996/0/319
Goodness-of-fit on <i>F</i> ²	0.969	1.003	0.872
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0318, <i>wR</i> ₂ = 0.0678	<i>R</i> ₁ = 0.0303, <i>wR</i> ₂ = 0.0679	<i>R</i> ₁ = 0.0377, <i>wR</i> ₂ = 0.0697
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0438, <i>wR</i> ₂ = 0.0700	<i>R</i> ₁ = 0.0390, <i>wR</i> ₂ = 0.0698	<i>R</i> ₁ = 0.0546, <i>wR</i> ₂ = 0.0733
Largest difference peak and hole (e Å ⁻³)	1.808 and -1.271	1.995 and -1.305	1.812 and -2.844

A CH₂Cl₂ solvent molecule was found in **6**. This was modelled as disordered over three sites, with the occupancies summed to 1.0. The carbon and chlorine atoms were given a common isotropic thermal parameter each, and the C–Cl distances restrained to be the same.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 217214–217221. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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References

- [1] (a) See for example S.E. Kabir, E. Rosenberg, L. Milone, R. Gobetto, D. Osella, M. Ravera, T. McPhillips, M.W. Day, D. Carlot, S. Hajela, E. Wolf, K. Hardcastle, *Organometallics* 16 (1997) 2674; (b) J.A. Cabeza, *Eur. J. Inorg. Chem.* (2002) 1559.
- [2] (a) See for example J.S. Song, S.H. Han, S.T. Nguyen, G.L. Geoffroy, A.L. Rheingold, *Organometallics* 9 (1990) 2386; (b) R.D. Adams, J.E. Babin, T.A. Wolfe, *Organometallics* 9 (1990) 440.
- [3] Q. Lin, W.K. Leong, *Organometallics* 22 (2003) 3639.
- [4] (a) K.A. Azam, A.J. Deeming, R.E. Kimber, P.R. Shukla, *J. Chem. Soc., Dalton Trans.* (1976) 1853; (b) A.J. Arce, Y. De Sanctis, A.J. Deeming, *J. Organomet. Chem.* 311 (1986) 371; (c) S.P. Tunik, I.A. Balova, M.E. Borovitev, E. Nordlander, M. Haukka, T.A. Pakkanen, *J. Chem. Soc., Dalton Trans.* (2002) 827.
- [5] (a) J.A. Barltrop, A.C. Day, C.J. Samuel, *J. Chem. Soc., Chem. Commun.* (1976) 822; (b) J.A. Barltrop, A.C. Day, C.J. Samuel, *J. Chem. Soc., Chem. Commun.* (1977) 598; (c) J.W. Pavlik, E.B. Keil, E.L. Sullivan, *J. Heterocyclic Chem.* 29 (1992) 1829; (d) P. Yates, I.W.J. Still, *J. Amer. Chem. Soc.* 85 (1963) 1208; (e) F.G. West, *Adv. Cycloaddition* 4 (1997) 1.
- [6] B.F.G. Johnson, R. Khattar, F.J. Lahoz, J. Lewis, P.R. Raithby, *J. Organomet. Chem.* 319 (1987) C51.
- [7] (a) O. Gambino, G.A. Vaglio, R.P. Ferrari, G. Cetini, *J. Organomet. Chem.* 30 (1971) 381; (b) G. Ferraris, G. Gervasio, *J. Chem. Soc., Dalton Trans.* (1974) 1813; (c) R.P. Ferrari, G.A. Vaglio, O. Gambino, M. Valle, G. Cetini, *J. Chem. Soc., Dalton Trans.* (1972) 1998.
- [8] (a) G. Ferraris, G. Gervasio, *J. Chem. Soc., Dalton Trans.* (1972) 1057; (b) R.P. Ferrari, G.A. Vaglio, *Trans. Metal Chem.* 8 (1983) 155.
- [9] (a) M.R. Burke, T. Funk, J. Takats, V.W. Day, *Organometallics* 13 (1994) 2109; (b) M.R. Burke, J. Takats, *J. Organomet. Chem.* 302 (1986) C25.
- [10] (a) O. Gambino, R.P. Ferrari, M. Chinone, G.A. Vaglio, *Inorg. Chim. Acta* 12 (1975) 155; (b) R.P. Ferrari, G.A. Vaglio, *Gazz. Chim. Ital.* 105 (1975) 939.
- [11] (a) A.W. Herlinger, A.L. Rheingold, *Acta Cryst. Sect. C* C53 (1997) 285; (b) N. Spetseris, J.R. Norton, C.D. Rithner, *Organometallics* 14 (1995) 603; (c) A.A. Cherkas, N. Hadj-Bagheri, A.J. Carty, E. Sappa, M.A. Pellinghelli, A. Tiripicchio, *Organometallics* 9 (1990) 1887; (d) A.J. Deeming, N.P. Randle, M.B. Hursthouse, R.L. Short, *J. Chem. Soc., Dalton Trans.* (1987) 2473; (e) A.A. Cherkas, A.J. Carty, E. Sappa, M.A. Pellinghelli, A. Tiripicchio, *Inorg. Chem.* 26 (1987) 3201; (f) G.L. Geoffroy, S. Rosenberg, A.W. Herlinger, A.L. Rheingold, *Inorg. Chem.* 25 (1986) 2916; (g) K.M. Motyl, J.R. Norton, C.K. Schauer, O.P. Anderson, *J. Amer. Chem. Soc.* 104 (1982) 7325.
- [12] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* (1987) S1.
- [13] K.L. Lu, M.L. Chung, P.Y. Lu, H.M. Gau, F.E. Hong, Y.S. Wen, *Organometallics* 13 (1994) 3177.
- [14] T. Asunta, K. Rissanen, V.V. Krivykh, M.I. Rybinskaya, *J. Organomet. Chem.* 372 (1989) 411.
- [15] A.J. Deeming, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry II*, vol. 7, Pergamon Press, 1995 (Chapter 12).
- [16] J.N. Nicholl, M.D. Vargas, *Inorg. Synth.* 28 (1989) 232.
- [17] M. Deng, W.K. Leong, *Organometallics* 21 (2002) 1221.
- [18] G.A. Vaglio, O. Gambino, R.P. Ferrari, G. Cetini, *Inorg. Chim. Acta* 7 (1973) 193.
- [19] SMART version 5.628, Bruker AXS Inc., Madison, WI, USA, 2001.
- [20] SAINT+ version 6.22a, Bruker AXS Inc., Madison, WI, USA, 2001.
- [21] G.M. Sheldrick, SADABS, 1996.
- [22] SHELXT L version 5.1, Bruker AXS Inc., Madison, WI, USA, 1997.
- [23] XHYDEX: A Program for Locating Hydrides in Metal Complexes, G. Orpen, School of Chemistry, University of Bristol, UK, 1997.