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Preliminary communication

STEPWISE SYNTHESIS OF $[Os_3(CO)_8(R_2C_2)(R'_2C_2)]$ FROM $[Os_3(CO)_{10}(R_2C_2)]$ UNDER MILD CONDITIONS, X-RAY CRYSTAL STRUCTURE OF $[Os_3(CO)_8(Ph_2C_2)_2]$; A BIS(ALKYNE) WITHOUT AN OSMACYCLOPENTADIENE RING

BRIAN F.G. JOHNSON, RAJESH KHATTAR, FERNANDO J. LAHOZ, JACK LEWIS* and PAUL R. RAITHBY

University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain)

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Summary

Treatment of a solution of $[Os_3(CO)_{10}(R_2C_2)]$ (R = Me (**1**), R = Ph (**2**)) in CH_2Cl_2 with $Me_3NO/MeCN$ in the presence of R'_2C_2 affords the new organometallic cluster $[Os_3(CO)_8(R_2C_2)(R'_2C_2)]$ (R = R′ = Me (**3**), R = R′ = Ph (**4**) and R = Ph, R′ = Me (**5**)). A single crystal X-ray analysis of compound **4** has established a triangular metal framework with both the alkyne units coordinated in a μ_3-η^2-$\|$-mode. In toluene, at 80°C, compound **4** undergoes rearrangement to the known compound, $[Os_3H(CO)_8(Ph_2C_2(Ph)C_2(C_6H_4))]$ (**6**) in which C–C bond formation has occurred to produce an osmacyclopentadiene ring.

Our continuing interest in alkyne-osmium clusters [1–3], and in particular C–C bond formation on a cluster template has prompted us to reinvestigate the reactions of $[Os_3(CO)_{10}(R_2C_2)]$ (R = Me (**1**), R = Ph (**2**)) with further alkynes by initial labilisation of the starting clusters with MeCN. This provides a convenient route to bis(alkyne) derivatives of triosmium clusters under mild conditions. A number of mono-, di-, tri- and tetra-nuclear species had been obtained by the thermal reactions of $[M_3(CO)_{12}]$ (M = Fe, Ru or Os) with alkynes [4–16]. Thermal reactions [8,9] of $[M_3(CO)_{12}]$ (M = Fe, Ru) with Ph_2C_2, initially give $[M_3(CO)_8(Ph_2C_2)_2]$ which exists in two isomeric forms: violet (M = Fe, Ru) and black (for M = Fe) or yellowish orange (for M = Ru). Both these isomers have different metal frameworks as well as different arrangements of organic units over this framework. In the violet isomer, the metal atoms define a triangle which is capped on both sides by the alkyne ligand (Fig. 1), and the alkyne groups remain separate. The violet isomer converts to the more thermodynamically stable black (for M = Fe) or yellowish orange (M = Ru) isomer in benzene, under reflux. In these clusters, the alkyne ligands have condensed together to form a metallacyclopentadiene ring and one M-M bond has been ruptured (Fig. 1).

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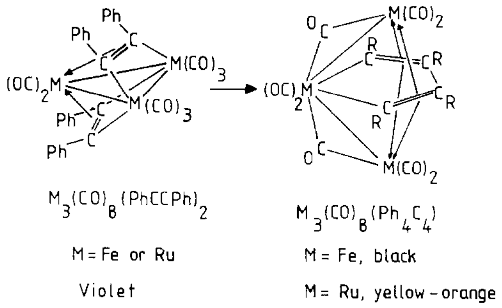

Fig. 1. Isomeric structures for $[M_3(CO)_8(Ph_2C_2)_2]$ (M = Fe, Ru), carbonyl ligands have been omitted for clarity.

In the thermal reaction of $[Os_3(CO)_{12}]$ with Ph_2C_2 in n-heptane, under reflux, a lemon-yellow, cluster, $[Os_3(CO)_8(Ph_2C_2)_2]$ (**6**) was produced as the initial product [11]. At first, **6** was considered to be isostructural to the violet isomers of $[M_3(CO)_8(Ph_2C_2)_2]$ (M = Fe or Ru), but, an X-ray single crystal structure analysis [14] has established **6** to be $[Os_3H(CO)_8(Ph_2C_2(Ph)C_2(C_6H_4))]$ (Fig. 2), with a structure based on an Os_3 triangle with the alkyne units linked via C–C bond

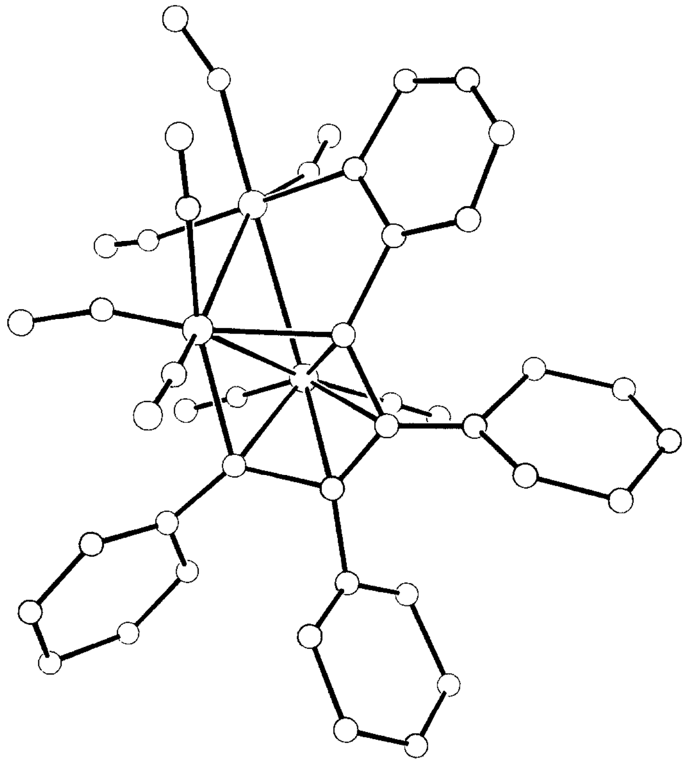

Fig. 2. The structure of $[Os_3H(CO)_8(Ph_2C_2(Ph)C_2(C_6H_4))]$ showing the osmacyclopentadiene ring.

formation to form part of an osmacyclopentadiene ring. Orthometallation of one of the phenyl rings has occurred, and the hydrogen has transferred to the metal framework. However, no isomer of $[Os_3(CO)_8(R_2C_2)_2]$ isostructural to the violet isomer of $[M_3(CO)_8(Ph_2C_2)_2]$ (M = Fe or Ru) has been reported so far. In this communication, we wish to report the synthesis and X-ray structure determination of a new isomer of $[Os_3(CO)_8(Ph_2C_2)_2]$ which is isostructural to the violet isomers of $[M_3(CO)_8(Ph_2C_2)_2]$ (M = Fe or Ru) and is a precursor to the lemon-yellow compound **6**.

Treatment of a CH_2Cl_2 solution of $[Os_3(CO)_{10}(R_2C_2)]$ [17] with Me_3NO (2.2 eq.) in the presence of a little MeCN and an excess of the appropriate alkyne (R'_2C_2), at −78°C, followed by subsequent warming to room temperature, affords the new cluster $[Os_3(CO)_8(R_2C_2)(R'_2C_2)]$ (R = R′ = Me (**3**), R = R′ = Ph (**4**) and R = Ph, R′ = Me (**5**)) in about 60-70% yield. This method provides a systematic preparation of mixed alkynes triosmium complexes under mild conditions. The products are readily purified by thin-layer chromatography (silica gel) using a 1/1 mixture of CH_2Cl_2/hexane as eluant. These clusters are obtained as air-stable orange or reddish orange crystals and have been fully characterised on the basis of their IR, ^1H NMR and mass spectroscopy (Table 1).

The IR spectra of compounds **3**–**5** in the terminal carbonyl region are very similar to each other but are different from those already reported for compound **6**. Both **4** and **6** exhibit the same molecular ions in their mass spectra and show the same stepwise loss of eight carbonyl groups. On the basis of spectroscopic evidence, **4** is believed to be another isomer of $[Os_3(CO)_8(Ph_2C_2)_2]$. In order to establish the molecular geometry of these products, a single crystal X-ray structure analysis of diphenylacetylene derivative **4** was carried out.

The molecular structure * of $[Os_3(CO)_8(Ph_2C_2)_2]$ (**4**) is shown in Fig. 3, which includes some important bond parameters. The irregular triangle of Os atoms is capped above and below by the two alkyne groups which both adopt the μ_3-η^2-$\|$-bonding mode. In this mode the alkyne-carbon atoms form σ-bonds to Os(1) and Os(3) and π-bonds to Os(2), with the acetylenic C≡C bonds parallel to Os(1)–Os(3) edge. The eight carbonyl groups are all terminal, two being coordinated to Os(2), and three each to Os(1) and Os(3). Overall, the structure is very similar to that previously observed for the violet isomer of the iron and ruthenium analogues, $[M_3(CO)_8(Ph_2C_2)_2]$ (M = Fe, Ru) [8,9], and may be viewed simply as a double substitution of $[Os_3(CO)_{12}]$ by diphenylacetylene, with the two alkynes remaining

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* *Crystal data*. $C_{36}H_{20}O_8Os_3$, $M = 1151.12$, monoclinic, space group $C2/c$ (No. 15), a 38.294(4), b 8.542(1), c 21.996(2) Å, β 114.66(1)°, V 6538.9 Å^3, D_c 2.338 g cm^{-3}, $Z = 8$, $F(000) = 4224$, λ(Mo-K_α) 0.71069 Å, μ(Mo-K_α) 116.65 cm^{-1}. Red multifacted blocks, crystal dimensions: 0.057 × 0.171 × 0.486 mm. 3883 data measured on a Stoe-Siemens four-circle diffractometer ($5.0 \leqslant 2\theta \leqslant 42.0°$), corrected for absorption, 2900 unique observed reflections with $|F| > 4\sigma(F)$. Structure solved by a combination of Patterson and Fourier difference techniques, and refined by full-matrix least squares, with Os and O atoms assigned anisotropic thermal parameters; phenyl H atoms fixed in idealised positions, and refined with one, overall common isotropic temperature factor. The weighting scheme employed was $2.106/[\sigma^2F + 0.000105F^2]$. The final residuals were $R = 0.030$ and $R_w = 0.028$.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA

Compound	ν(CO) (cm^{-1}) [a]	^{1}H NMR [b] (δ, ppm)	Analysis (Found (Calcd.) (%))		Molecular weight [c] (mass spectral) (m/e)
			C	H	
$[Os_3(CO)_8(MeC_2)_2]$	2080(s), 2042(vs), 2022(s), 2008(vs), 1970(s), 1934(m)	3.40(s, 12H)	–	–	908
$[Os_3(CO)_8(Ph_2C_2)_2]$	2116(vw), 2084(s), 2049(vs), 2025(s,sh), 2017(vs), 1994(w) 1981(m), 1946(m)	7.20(m, 20H)	36.92 (37.54)	2.00 (1.73)	1156
$[Os_3(CO)_8(Ph_2C_2)(Me_2C_2)]$	2082(s), 2046(vs), 2025(s), 2013(vs), 1988(w,sh), 1976(m), 1940(w)	7.22(m, 10H) 3.54(s, 6H)	29.57 (30.39)	1.60 (1.55)	1032
$[Os_3H(CO)_8(Me_2C_2(Ph)C_2(C_6H_4))]$	2093(s), 2055(s), 2027(vs), 2012(m), 1990(m), 1975(w)	7.00(m, 9H) 2.81(s, 3H) 2.54(s, 3H) −14.62(s, 1H)	30.42 (30.39)	1.64 (1.55)	1032

[a] In CH_2Cl_2. [b] In CD_2Cl_2. [c] Based on ^{192}Os.

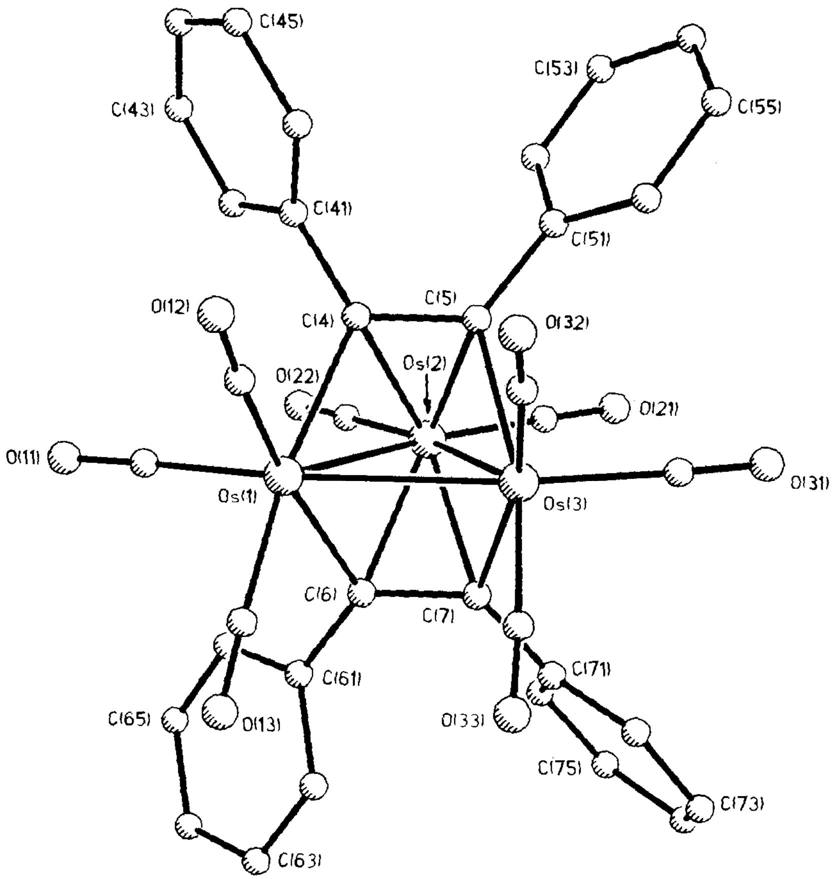
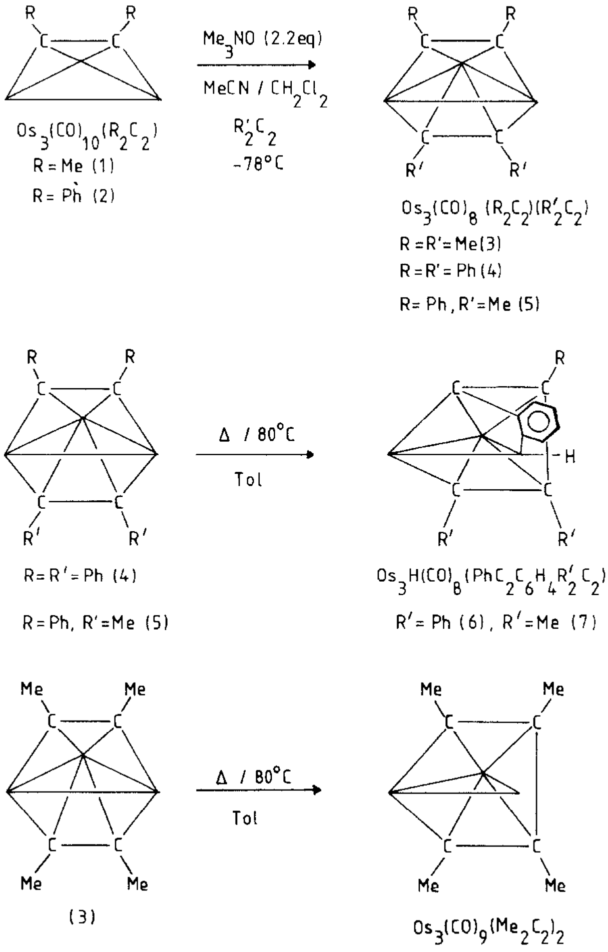


Fig. 3. The molecular structure of $[Os_3(CO)_8(Ph_2C_2)_2]$ (4) showing the atom numbering scheme adopted. Bond lengths: Os(2)–Os(1), 2.690(1); Os(3)–Os(1), 2.759(1); Os(3)–Os(2), 2.704(1); C(4)–Os(1), 2.191(11); C(6)–Os(1), 2.210(10); C(4)–Os(2), 2.149(10); C(5)–Os(2), 2.152(10); C(6)–Os(2), 2.127(10); C(7)–Os(2), 2.150(10); C(5)–Os(3), 2.180(10); C(7)–Os(3), 2.177(10); C(5)–C(4), 1.440(13); C(41)–C(4), 1.494(14); C(51)–C(5), 1.491(14); C(7)–C(6), 1.406(13); C(61)–C(6), 1.475(14); C(71)–C(7), 1.500(13) Å. Bond angles: Os(3)–Os(1)–Os(2), 59.5(1); Os(3)–Os(2)–Os(1), 61.5(1); Os(2)–Os(3)–Os(1), 59.0(1); C(6)–Os(1)–C(4), 101.3(4); C(5)–Os(2)–Os(4), 39.1(3); C(6)–Os(2)–C(4), 101.3(4); C(5)–Os(2)–Os(4), 39.1(3); C(6)–Os(2)–C(4), 105.4(4); C(6)–Os(2)–C(5), 118.1(4); C(7)–Os(2)–C(4), 117.9(4); C(7)–Os(2)–C(5), 103.4(4); C(7)–Os(2)–Os(6), 38.4(3); C(7)–Os(3)–C(5), 101.6(4); Os(2)–C(4)–Os(1), 76.6(3); C(5)–C(4)–Os(1), 108.0(7); C(5)–C(4)–Os(2), 70.5(6); C(41)–C(4)–Os(1), 125.6(7); C(41)–C(4)–Os(2), 134.3(7); C(41)–C(4)–C(5), 123.3(9); Os(3)–C(5)–Os(2), 77.3(3); C(4)–C(5)–Os(2), 70.3(6); C(4)–C(5)–Os(3), 107.1(7); C(51)–C(5)–Os(2), 126.2(7); C(51)–C(5)–Os(3), 127.3(7); C(51)–C(5)–Os(3), 127.3(7); C(51)–C(5)–C(4), 124.6(9); Os(2)–C(6)–Os(1), 76.6(3); C(7)–C(6)–Os(1), 108.3(7); C(7)–C(6)–Os(2), 71.7(6); C(61)–C(6)–Os(1), 122.6(6); C(61)–C(6)–Os(2), 133.8(7); C(61)–C(6)–C(7), 125.9(9); Os(3)–C(7)–Os(2), 77.4(3); C(6)–C(7)–Os(2), 128.2(7); C(71)–C(7)–Os(3), 126.4(7); C(71)–C(7)–C(6), 124.7(9)°.

separate entities. If the acetylenic carbon atoms are included in the cluster framework, the polyhedron may be described as two fused square based pyramids sharing a common triangular face.

All three Os–Os distances in the structure of 4 are significantly shorter than the comparative distances in the parent cluster $[Os_3(CO)_{10}(Ph_2C_2)]$ [18] (2.711(1), 2.888(1), and 2.844(1) Å), and in both these acetylenic clusters the average Os–Os distances are shorter than the value of 2.877(3) Å in the binary carbonyl, $[Os_3(CO)_{12}]$, itself [19]. This indicates that a capping alkyne group exerts a bond shortening influence on a metal triangle, and this influence increases with increasing alkyne substitution. The acetylenic C–C distances in **4** are not significantly different from the distance of 1.44(1) Å in $[Os_3(CO)_{10}(Ph_2C_2)]$ [18], and in both cases this indicates a reduction in the formal C–C bond order upon coordination of the alkynes to the metal template.

Compound **4** in toluene, at 80°C, undergoes isomerisation to form the known compound **6** in which the two diphenylacetylene units couple with each other to form an osmacyclopentadiene ring and the *ortho*-metallation of one of the phenyl rings also occurs. This isomerisation may have occurred by cleavage of two M–C(alkyne) bonds together with formation of a C(alkyne)–C(alkyne) bond to generate an osmacyclopentadiene ring (Scheme 1). This reaction is quite different



from the iron and ruthenium analogues, in which case the condensation of alkynes has resulted in rupture of one of the metal–metal bonds, and adds further support to one of our previous findings [20] that metal–metal bonds in osmium clusters are stronger than in their iron and ruthenium analogues. In a similar manner to **4**, **5** is slowly converted into $[Os_3H(CO)_8(Me_2C_2(Ph)C_2(C_6H_4))]$ (**7**) in CH_2Cl_2, at room temperature over a few days. The thermolysis of **3** in toluene, at 80°C, yields the known violet compound, $[Os_3(CO)_9(Me_2C_2)_2]$ [13]. These reactions are shown in Scheme 1.

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