Journal of Organometallic Chemistry, 386 (1990) 121–137
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20571

Synthesis and solution studies of $Os_3(CO)_9L(R_2C_2)$ (L = CO, MeCN, $P(OMe)_3$ or PPh_3); crystal and molecular structure of $Os_3(CO)_9P(OMe)_3(Ph_2C_2)$

Mark A. Gallop, Brian F.G. Johnson, Rajesh Khattar, Jack Lewis, and Paul R. Raithby

University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (U.K.)

(Received October 9th, 1989)

Abstract

Reaction of $Os_3(CO)_{10}(R_2C_2)$ (R = Ph, Et or Me) with 1.1 equivalent of Me_3NO in the presence of MeCN at $-78\,^{\circ}C$ produces a labilized cluster, $Os_3(CO)_9(NCMe)(R_2C_2)$, which upon reaction with alkyne (R'_2C_2) affords the known violet complex of formula $Os_3(CO)_9(R_2C_2)(R'_2C_2)$, in which both the alkyne molecules are linked via a carbon–carbon bond to produce an osmacyclic ring. With simple phosphorus donor ligands L (where L = $P(OMe)_3$, PPh_3), the cluster $Os_3(CO)_9(NCMe)(R_2C_2)$ affords the corresponding substituted complex $Os_3(CO)_9L(R_2C_2)$ in yields of up to 80% yields. The structure of $Os_3(CO)_9P(OMe)_3(Ph_2C_2)$ has been established by a single crystal X-ray study. The structure is based on a triangular metal framework with the diphenylacetylene ligand bonded in a μ_3-η^2-$\|$-bonding mode, forming two σ- and a π-bond with the osmium atoms, a $P(OMe)_3$ ligand being attached to one osmium bearing a σ-bonded acetylenic carbon and occupying a pseudo equatorial position. ^{13}C NMR studies have been carried out on the complex $Os_3(CO)_9L(Me_2C_2)$ (L = CO, $P(OMe)_3$ or PPh_3) to give information about the structure in solution. The carbonyl ligands in all of these complexes are fluxional, and an intramolecular mechanism by which the carbonyls interchange between the three osmium atoms, in each complex, is discussed in detail.

Introduction

The rich and beautiful chemistry of metal carbonyl clusters with alkynes has attracted considerable attention [1,2]. This has resulted in the preparation of complexes exhibiting a wide variety of novel coordination modes, which serve as good models for the chemisorption of small hydrocarbon molecules on metal surfaces [3]. The synthetic routes to alkyne-containing metal clusters are now well developed. The preferred route to these clusters involves chemical activation of the

0022-328X/90/$03.50

cluster rather than thermal or photochemical activation. The structures and bonding aspects of metal clusters containing alkyne ligands have been the subject of many recent publications [4–7]. Within the alkyne-trimetallic cluster family, two types of alkyne bonding modes have been observed. The alkyne ligand has been found either in μ_3-η^2-$\|$- or μ_3-η^2-$\perp$-bonding modes, though the former is more common. The μ_3-η^2-$\|$-bonding mode has been observed in a number of complexes of the type $Os_3(CO)_{10}(R_2C_2)$, $H_2M_3(CO)_9(R_2C_2)$ (M = Ru or Os) [8–10], whereas μ_3-η^2-$\perp$-bonding has been observed in $Fe_3(CO)_9(Ph_2C_2)$ [11], $Fe_2Ru(CO)_9(Ph_2C_2)$ [4] and more recently in $Os_3(CO)_7(Ph_2PCH_2PPh_2)(Ph_2C_2)$ [12]. Electronic factors are believed to be responsible for the adoption of different alkyne coordination modes in these complexes [4,6]. Less attention has been given to solution studies of metal clusters containing alkyne ligands [13–15], although a recent paper has discussed the relationship between structure and ligand dynamics in a number of $Os_3(CO)_9$(alkyne)(L) (L = CO, PR_3) systems [16]. The information regarding the structures of these clusters in solution can be obtained from ^1H and ^{13}C NMR spectroscopy. In this paper we report the synthesis and solution studies of $Os_3(CO)_9L(R_2C_2)$ (L = CO, MeCN, $P(OMe)_3$ or PPh_3), together with the crystal and molecular structure of the phosphite derivative.

Results and discussion

The clusters $Os_3(CO)_{10}(R_2C_2)$ (**1**: R = Ph; **2**: R = Et or **3**: R = Me) were initially reported by Shapley and coworkers [17] from the activated acetonitrile complexes $Os_3(CO)_{12-n}(NCMe)_n$ (n = 1 or 2). For Ph_2C_2, the major product of the reaction is **1** (80% yield), while for Et_2C_2 and Me_2C_2, two products are formed. One of them is a yellowish-orange complex of formula $Os_3(CO)_{10}(R_2C_2)$ (**2**: R = Et or **3**: R = Me) (42% yield) and the other is a dirty-red complex of formula $Os_3(CO)_9(R_2C_2C(O)R_2C_2)$ (25% yield). The latter complex was initially obtained by Deeming from the reaction of $H_2Os_3(CO)_{10}$ with alkyne [8]. The IR spectrum of **1** shows no band due to a bridging carbonyl ligand and is consistent with the solid state crystal structure [10,17], whereas the derivatives **2** and **3** each show a weak and broad band in the 1850 cm^{-1} region, suggesting the presence of a bridging carbonyl ligand [8].

Treatment of the complexes **1**–**3** with equimolar amounts of Me_3NO in the presence of a little MeCN at −78°C followed by slow warming to room temperature affords a new activated cluster that has been tentatively formulated as $Os_3(CO)_9(NCMe)(R_2C_2)$ (**4**: R = Ph; **5**: R = Et or **6**: R = Me). Complex **4** shows IR bands only in the terminal carbonyl region, whereas the complexes **5** and **6** exhibit bands in the terminal and bridging carbonyl region (Table 1), suggesting the parent compounds and their derivatives have analogous structures. It was not possible to obtain the electron impact mass spectrum of the clusters **4**–**6** as they all decomposed in the spectrometer. The ^1H NMR spectrum of **4** exhibits a broad singlet at δ 2.44 due to a coordinated acetonitrile ligand, whereas the ^1H NMR spectra of **5** and **6** show that the clusters have decomposed to regenerate the starting materials **2** and **3** respectively, possibly by scavenging CO. Consistent with this observation are the reactions of CO with CH_2Cl_2 solutions of **4**–**6**, which produce quantitative yields of **1**–**3**. The cluster **4** reacts with molecular hydrogen to give the known cluster, $H_2Os_3(CO)_9(Ph_2C_2)$ [8], where the hydride ligands are believed to bridge an Os–Os edge. Reactions of the clusters **4**–**6** with further alkynes R'_2C_2

Table 1

Spectroscopic data for some alkyne-substituted triosmium derivatives

Compound	IR spectrum [a] (ν(CO) (cm^{-1}))	Mass spectrum [b] (m/e)	^{1}H NMR spectrum [c] (δ)
$Os_3(CO)_9(NCMe)(Ph_2C_2)$ (**4**)	2078(m), 2047(vs), 2026(vs), 2000(m), 1982(m), 1956(w) 1935(w).	[d]	2.44 (s, 3H) 7.1 (m, 10H)
$Os_3(CO)_9(NCMe)(Et_2C_2)$ (**5**)	2067(m), 2040(vs), 2019(vs), 1993(m), 1978(m,sh), 1954(w,sh), 1932(w,sh), 1855(vw,br).	[d]	–
$Os_3(CO)_9(NCMe)(Me_2C_2)$ (**6**)	2075(m), 2042(vs), 2019(vs), 1993(s), 1978(s,sh), 1952(m), 1929(m), 1846(w,br).	[d]	–
$Os_3(CO)_9P(OMe)_3(Ph_2C_2)$ (**7**)	2079(m), 2038(vs), 2028(s), 1999(s), 1978(m,br).	1130	3.48 (d, 9H) ^3J(P–H) 12 Hz 6.9 (m, 10H)
$Os_3(CO)_9PPh_3(Et_2C_2)$ (**8**)	2108(vw), 2071(m), 2033(vs), 2005(m), 1995(m), 1976(m), 1942 (w).	[d]	3.38 (m, 1H) 2.98 (m, 2H) 2.30 (m, 1H) 1.38 (t, 6H) 7.65 (m, 15H)
$Os_3(CO)_9P(OMe)_3(Me_2C_2)$ (**9**)	2077(m), 2036(vs), 2023(s), 1994(s), 1976(m, sh), 1846(vw, br).	1006	3.72 (d, 9H) [e] ^3J(P–H) 12.2 Hz 2.38 (s, 3H) 2.35 (s, 3H)

[a] In CH_2Cl_2. [b] Based on ^{192}Os. [c] In CD_2Cl_2. [d] Parent peak not observed. [e] In $CDCl_3$.

(R′ = Ph or Me) afford the known metallacyclic species, $Os_3(CO)_9(R_2C_2)(R'_2C_2)$, in which both the alkynes are linked via a carbon–carbon bond [18]. The latter cluster was initially obtained from the thermolysis of $Os_3(CO)_{10}(Ph_2C_2)$ with Ph_2C_2 [19]. The advantage of this synthetic approach over the thermolysis is that it allows considerable control over the formation of a carbon–carbon bond. This synthetic route also offers a systematic high yield synthesis of mixed alkyne metallacyclic species under relatively mild conditions. The acetonitrile ligand in the complexes **4**–**6** can be easily displaced by simple phosphorus donor ligands such as phosphite or phosphine to produce the substituted derivatives, $Os_3(CO)_9P(OMe)_3(R_2C_2)$ (**7**: R = Ph or **9**: R = Me) and $Os_3(CO)_9PPh_3(Et_2C_2)$ (**8**). The complexes **7**–**9** have been characterized on the basis of IR, mass and ^{1}H NMR spectroscopic data (Table 1). The complexes **7**–**9** exhibit IR patterns very similar to that for the acetonitrile derivatives **4**–**6**, indicating that a simple substitution has taken place. We failed to obtain X-ray quality crystals of any one of the acetonitrile derivatives **4**–**6**, but have established the structure of one phosphite derivative **7** which is discussed below.

The ^{1}H NMR spectrum of **9** shows a doublet at δ 3.72 (^3J(P–H) 12.2 Hz) and two singlets of equal intensity, one at δ 2.38 and another at 2.35. The doublet at δ 3.72 is assigned to a coordinated $P(OMe)_3$ group, whereas the two singlets are assigned to two inequivalent methyl groups. It is noteworthy that only one isomer is obtained in this case, even though a number of isomeric structures are possible. The ^{31}P{^{1}H} NMR spectrum of **9** shows a singlet at δ −37.26 (referenced to TMP) due

Table 2

Bond lengths (Å) in $Os_3(CO)_9P(OMe)_3(Ph_2C_2)$

Os(1)–Os(2)	2.885(1)	Os(1)–Os(3)	2.827(1)
Os(1)–P(1)	2.313(4)	Os(1)–C(11)	1.960(16)
Os(1)–C(12)	1.969(13)	Os(1)–C(13)	1.995(13)
Os(1)–C(10)	2.161(13)	Os(2)–Os(3)	2.706(1)
Os(2)–C(21)	1.947(18)	Os(2)–C(22)	1.937(18)
Os(2)–C(23)	1.883(14)	Os(2)–C(20)	2.083(11)
Os(3)–C(31)	1.871(19)	Os(3)–C(32)	1.921(12)
Os(3)–C(33)	1.921(17)	Os(3)–C(10)	2.214(13)
Os(3)–C(20)	2.312(11)	P(1)–O(1)	1.524(12)
P(1)–O(2)	1.585(11)	P(1)–O(3)	1.548(19)
O(1)–C(1)	1.449(28)	O(2)–C(2)	1.391(27)
O(3)–C(3)	1.405(37)	C(11)–O(11)	1.089(20)
C(12)–O(12)	1.124(16)	C(13)–O(13)	1.113(17)
C(21)–O(21)	1.096(24)	C(22)–O(22)	1.131(21)
C(23)–O(23)	1.154(17)	C(31)–O(31)	1.158(24)
C(32)–O(32)	1.134(16)	C(33)–O(33)	1.138(20)
C(10)–C(20)	1.432(18)	C(10)–C(101)	1.511(15)
C(20)–C(201)	1.515(15)		

to a coordinated $P(OMe)_3$ group. The ^1H NMR spectrum of 7 shows a doublet at δ 3.48(^3J(P–H) 12 Hz) due to a coordinated $P(OMe)_3$ group and a multiplet in the region δ 7.0–6.78 due to phenyl protons.

The structure of 7 has been established by a single crystal X-ray study. Suitable single crystals of 7 were grown by the slow evaporation of a CH_2Cl_2/hexane solution at −5 °C during 2 days. The molecular structure of 7 is illustrated in Fig. 1, and lists of bond lengths and angles are presented in Tables 2 and 3, respectively. The three osmium atoms define an irregular triangle which is asymmetrically capped

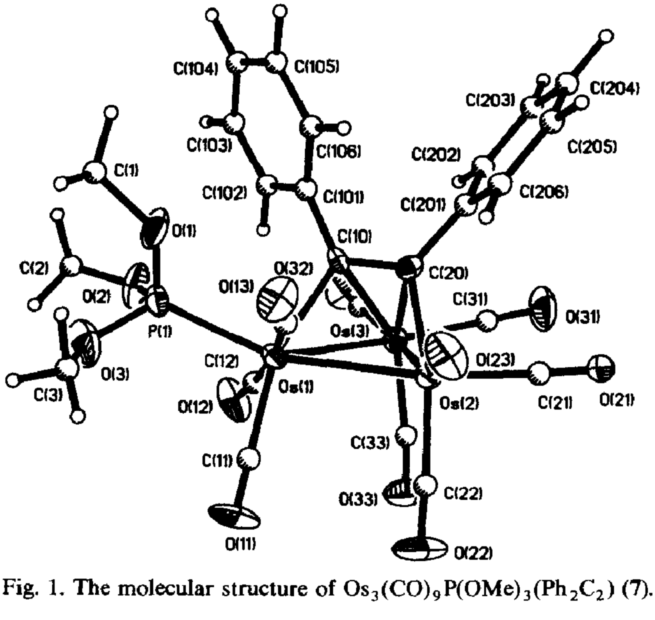

Fig. 1. The molecular structure of $Os_3(CO)_9P(OMe)_3(Ph_2C_2)$ (7).

Table 3

Bond angles (°) in $Os_3(CO)_9P(OMe)_3(Ph_2C_2)$.

Os(3)-Os(1)-Os(2)	56.5(1)	P(1)-Os(1)-Os(2)	152.8(1)
P(1)-Os(1)-Os(3)	133.2(1)	C(11)-Os(1)-Os(2)	90.6(5)
C(11)-Os(1)-Os(3)	116.9(5)	C(11)-Os(1)-P(1)	101.4(5)
C(12)-Os(1)-Os(2)	117.9(5)	C(12)-Os(1)-Os(3)	68.8(5)
C(12)-Os(1)-P(1)	86.9(5)	C(12)-Os(1)-C(11)	89.2(6)
C(13)-Os(1)-Os(2)	68.0(5)	C(13)-Os(1)-Os(3)	115.7(5)
C(13)-Os(1)-P(1)	87.1(5)	C(13)-Os(1)-C(11)	91.9(6)
C(13)-Os(1)-C(12)	174.0(7)	C(10)-Os(1)-Os(2)	69.5(3)
C(10)-Os(1)-Os(3)	50.6(3)	C(10)-Os(1)-P(1)	97.5(4)
C(10)-Os(1)-C(11)	160.1(6)	C(10)-Os(1)-C(12)	98.1(5)
C(10)-Os(1)-C(13)	82.8(5)	Os(3)-Os(2)-Os(1)	60.6(1)
C(21)-Os(2)-Os(1)	157.2(4)	C(21)-Os(2)-Os(3)	96.7(4)
C(22)-Os(2)-Os(1)	94.7(6)	C(22)-Os(2)-Os(3)	102.8(5)
C(22)-Os(2)-C(21)	93.0(7)	C(23)-Os(2)-Os(1)	108.6(6)
C(23)-Os(2)-Os(3)	157.2(4)	C(23)-Os(2)-C(21)	91.5(7)
C(23)-Os(2)-C(22)	98.0(6)	C(20)-Os(2)-Os(1)	70.0(4)
C(20)-Os(2)-Os(3)	55.9(3)	C(20)-Os(2)-C(21)	95.8(6)
C(20)-Os(2)-C(22)	157.8(5)	C(20)-Os(2)-C(23)	102.2(5)
Os(2)-Os(3)-Os(1)	62.8(1)	C(31)-Os(3)-Os(1)	158.8(4)
C(31)-Os(3)-Os(2)	98.1(4)	C(32)-Os(3)-Os(1)	106.9(5)
C(32)-Os(3)-Os(2)	167.9(5)	C(32)-Os(3)-C(31)	90.9(7)
C(33)-Os(3)-Os(1)	97.4(6)	C(33)-Os(3)-Os(2)	89.7(4)
C(33)-Os(3)-C(31)	91.3(7)	C(33)-Os(3)-C(32)	98.2(6)
C(10)-Os(3)-Os(1)	48.9(3)	C(10)-Os(3)-Os(2)	72.6(3)
C(10)-Os(3)-C(31)	119.1(6)	C(10)-Os(3)-C(32)	96.0(5)
C(10)-Os(3)-C(33)	146.1(6)	C(20)-Os(3)-Os(1)	68.5(4)
C(20)-Os(3)-Os(2)	48.3(3)	C(20)-Os(3)-C(31)	92.1(6)
C(20)-Os(3)-C(32)	123.7(5)	C(20)-Os(3)-C(33)	137.9(5)
C(20)-Os(3)-C(10)	36.8(5)	O(1)-P(1)-Os(1)	111.2(5)
O(2)-P(1)-Os(1)	111.1(5)	O(2)-P(1)-O(1)	110.2(6)
O(3)-P(1)-Os(1)	121.9(6)	O(3)-P(1)-O(1)	107.3(8)
O(3)-P(1)-O(2)	93.8(8)	C(1)-O(1)-P(1)	130.1(13)
C(2)-O(2)-P(1)	129.9(13)	C(3)-O(3)-P(1)	118.3(21)
O(11)-C(11)-Os(1)	176.5(13)	O(12)-C(12)-Os(1)	169.4(15)
O(13)-C(13)-Os(1)	167.3(15)	O(21)-O(21)-Os(2)	176.9(13)
O(22)-C(22)-Os(2)	174.1(15)	O(23)-C(23)-Os(2)	177.3(16)
O(31)-C(31)-Os(3)	179.3(13)	O(32)-C(32)-Os(3)	173.1(13)
O(33)-C(33)-Os(3)	174.1(17)	Os(3)-C(10)-Os(1)	80.5(4)
C(20)-C(10)-Os(1)	107.2(8)	C(20)-C(10)-Os(3)	75.3(7)
C(101)-C(10)-Os(1)	124.7(9)	C(101)-C(10)-Os(3)	129.9(7)
C(101)-C(10)-C(20)	123.4(10)	Os(3)-C(20)-Os(2)	75.8(4)
C(10)-C(20)-Os(2)	112.0(9)	C(10)-C(20)-Os(3)	67.9(6)
C(201)-C(20)-Os(2)	125.3(8)	C(201)-C(20)-Os(3)	122.0(8)
C(201)-C(20)-C(10)	122.6(10)	C(102)-C(101)-C(10)	120.8(7)
C(106)-C(101)-C(10)	118.9(7)	C(202)-C(201)-C(20)	123.6(7)
C(206)-C(201)-C(20)	116.3(8)		

by a diphenylacetylene unit. The alkyne ligand forms a σ-bond to Os(1) and Os(2), and a π-bond to Os(3) and donates four electrons to the cluster unit. All the nine carbonyl ligands are terminally bonded and are symmetrically arranged over three osmium atoms. A trimethyl phosphite ligand is attached to Os(1) in the pseudo-equatorial position.

The overall molecular structure of 7 is similar to that of the parent complex $Os_3(CO)_{10}(Ph_2C_2)$ [10], and of the related derivatives, $Os_3(CO)_{10}(Et_2C_2)$ and $Os_3(CO)_9PPh_3(Et_2C_2)$ [16]. The Os–Os distances show the same trends in all four complexes, with the longest Os–Os edge being approximately parallel to the alkyne C–C vector (the Os(1)–Os(2) edge in 7). In each case, the Os–Os edge between the two Os atoms with three carbonyls bonded to them is the shortest (Os(2)–Os(3) in 7), and the third edge is intermediate in length (Os(1)–Os(3) in 7). In all the complexes the coordination of the alkyne, regardless of the nature of the substituents is slightly asymmetric, with, in the case of 7, the C(10)–C(20) vector making an angle of 8.6° with the Os(1)–Os(2) edge, showing the twisting of the ligand away from a truly parallel alignment. This is reflected in the slightly longer Os–C σ-bonded distance to the metal atom coordinated to four carbonyl or phosphorus donor ligands compared with that to the oneσ-bonded to three, and in a concomitant shortening of the π-bonds in the reverse order.

In terms of the formal electron count, with the alkyne ligand acting as a four electron donor, Os(3) is electron precise, with an electron count of 18, whereas Os(1) is electron rich with an electron count of 19 and Os(2) is electron deficient with an electron count of 17. This electronic imbalance, which is formally present in all four compounds, is partially alleviated by the presence of incipient bridging carbonyl ligands. In complex 7 the two carbonyls C(12)O(12) and C(13)O(13) bend towards Os(3) and Os(2) respectively (Os(2)...C(13) 2.826(17) Å, Os(1)–C(13)–O(13) 167.3(15)°; Os(3)...C(12) 2.802(19) Å, Os(1)–C(12)–O(12) 169.4(15)°) and donate electron density to them. Similar incipient bridging distances are observed in $Os_3(CO)_{10}(Ph_2C_2)$ [10] and $Os_3(CO)_9PPh_3(Et_2C_2)$ [16], but in $Os_3(CO)_{10}(Et_2C_2)$ [16] one of these bridging distances is much shorter (2.302(18) Å), and this carbonyl may be considered as truly bridging. In the context of the discussion below of the fluxional processes involving the carbonyl ligands in these clusters, the various distances for the semi-bridging carbonyls may represent steps along the pathway of a dynamic process involving terminal to bridge exchange.

The most interesting comparison between the structure of 7 and that of the triphenylphosphine derivative, $Os_3(CO)_9PPh_3(Et_2C_2)$ [16], is that the position taken up by the phosphorus donor ligand is different in the two cases. In 7, the phosphite ligand is *pseudo-trans* to the Os(1)–Os(2) edge (P(1)–Os(1)–Os(2) 152.8(1)°) and makes an angle of 97.5(4)° with the acetylenic carbon atom, C(10), while in the phosphine derivative the P–Os–C(acetylene) angle is 159.9(2)°, with

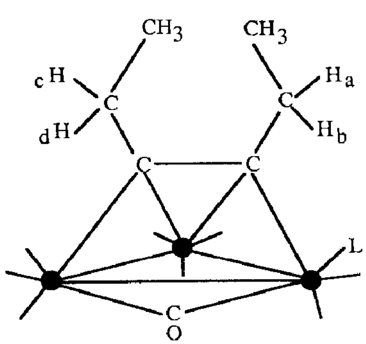

Fig. 2. Structure of $Os_3(CO)_9L(Et_2C_2)$ (L = CO (**2**) or PPh_3 (**8**)).

the triphenylphosphine occupying a position which is *pseudo-trans* to this carbon. For $Os_3(CO)_9PPh_3(Et_2C_2)$ [16], the phosphine does make an angle of 150.44(6)° with the equivalent Os(1)–Os(3) edge. The difference in orientation of the phosphite and phosphine in the two complexes may reflect the different steric requirements of the two ligands but also may be dependent on the nature of the substituents on the alkyne and on their orientations.

The ^1H NMR spectrum of **8** exhibits broad multiplets at δ 3.38, 2.98, 2.30 and a triplet at 1.38 in the ratio of 1/2/1/6. The triplet at δ 1.38 is due to the methyl protons of the diethylacetylene unit. The multiplets at δ 3.38, 2.98 and 2.30 must be due to the methylene protons of the diethylacetylene unit. Four multiplets are expected for the two pairs of diastereotopic methylene protons H^a/H^b and H^c/H^d (Fig. 2), though a superimposition of multiplets at δ 2.98 reduces the number of resolved methylene resonances to three. These results suggest that the diethylacetylene moiety in this complex is rigid in solution.

The methylene protons are also diastereotopic in the parent cluster **2**. Its ^1H NMR spectrum shows multiplets at δ 2.78 and 2.23 in a 1/1 ratio and a triplet at δ 1.15. In this case, although the methylene protons are diastereotopic, the protons H^a, H^c and H^b, H^d are equivalent due to symmetry in the molecule. Selective decoupling experiments have been carried out to measure the exact coupling constants for the methylene protons. In the case of **2**, irradiation at δ 1.15 reduces the multiplets at δ 2.78 and 2.23 into doublets with a coupling constant of ca. 13.4 Hz respectively. A similar situation exists in the clusters $Os_6(CO)_{16}(Et_2C_2)$ [20] and $CpNiCoM(CO)_6(Et_2C_2)$ [15] (M = Fe, Ru or Os) where the methylene protons are also diastereotopic and coupling constants of ca. 15 Hz have been measured.

The non-rigid behavior of these clusters in solution was examined by variable temperature ^{13}C NMR spectroscopic studies, and the results were as shown below, generally in agreement with those reported previously for closely related systems [16]. The complexes chosen for the spectroscopic study were $Os_3(CO)_9L(Me_2C_2)$ (**3**: L = CO; **9**: R = $P(OMe)_3$; **10**: R = PPh_3) containing ^{13}CO (ca. 40% ^{13}C).

^{13}C NMR study of $Os_3(CO)_{10}(R_2C_2)$ (2: R = Et or 3: R = Me)

The ^{13}C NMR spectrum of $Os_3(CO)_{10}(Et_2C_2)$ (**2**) consists of two resonances: a singlet at δ 151.8 and a broad singlet at δ 177.3. The singlet at δ 151.8 is assigned to the equivalent alkynic carbons. The broad singlet at δ 177.3 must be due to the carbonyl ligands, which seem to be fluxional at room temperature. A similar situation exists in the case of $Os_3(CO)_{10}(Me_2C_2)$ (**3**), where the alkynic carbons are located at δ 142.1 and the fluxional carbonyl ligands show a broad resonance at δ 179.0. The fluxional behavior of the carbonyl ligands in this complex was investigated by variable temperature ^{13}C NMR studies. An enriched (^{13}CO) sample of **3** was synthesised by reaction of $Os_3(^{13}CO)_{10}(NCMe)_2$ with Me_2C_2. The ^{13}C NMR spectrum of **3** recorded at various temperatures is shown in Fig. 3. At 183 K, the spectrum consists of six singlet resonances forming a 1/2/1/2/2/2 pattern in the δ 170–215 region due to the carbonyl ligands. The low-field resonance at δ 210.3 is tentatively assigned to a bridging carbonyl ligand. The remaining five resonances are assigned to the terminal carbonyl ligands. ^{187}Os satellites (at the natural abundance level, 1.64%, $I = 1/2$) in the ^{13}C NMR spectrum have also been observed and the corresponding nuclear spin–spin coupling constants ($^1J(Os{-}C)$) are recorded in Table 4, together with their probable assignments. For the bridging

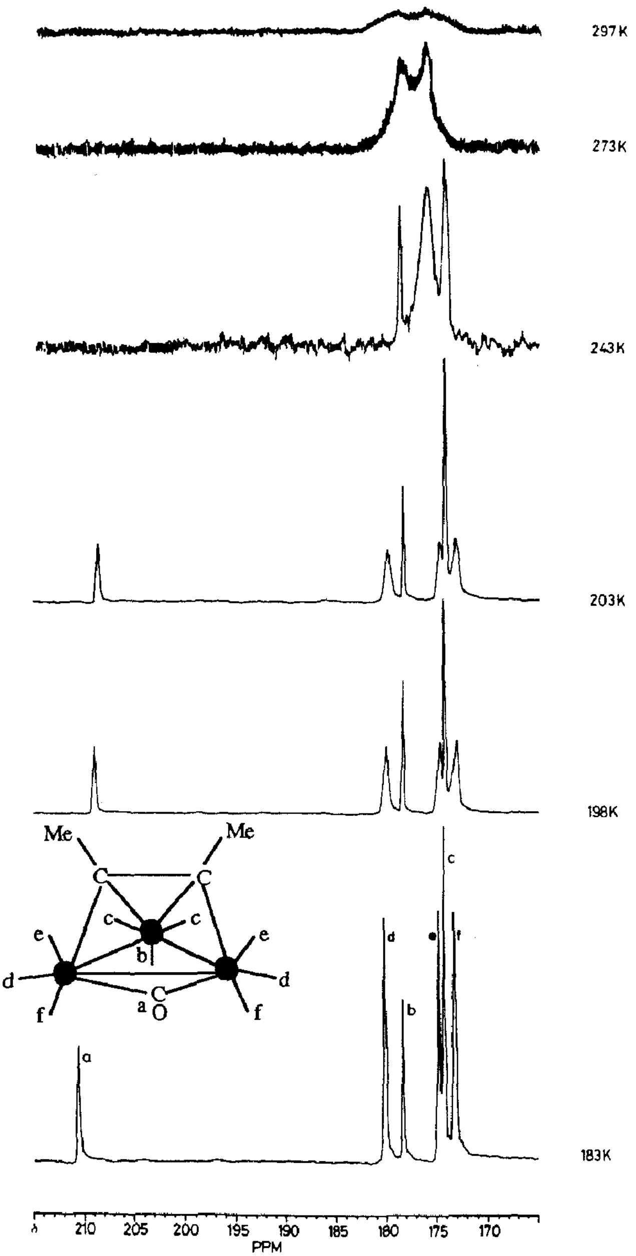

Fig. 3. ^{13}C NMR spectra of $Os_3(^{13}CO)_{10}(Me_2C_2)$ (3) recorded at different temperatures.

carbonyl ligand, CO^a, $^1J(^{187}Os-^{13}C)$ is ca. 45 Hz, whereas for other terminally bonded carbonyl ligands in **3** (both axial and equatorial), it ranges from 107 to 128 Hz (Table 4) and is comparable to the values reported previously in a number of osmium carbonyl clusters [21,22]. It was not possible to observe ^{187}Os satellites in the ^{13}C NMR spectrum for the resonances δ 174.5 and 174.1 owing to their close chemical shifts, which means that the satellites are hidden under the neighbouring resonances.

Table 4

Nuclear spin–spin coupling constants ($^1J(^{187}Os-^{13}C)$) for some alkyne-substituted triosmium clusters

Clusters	Chemical shift (δ)	Assignment of carbonyl ligands	$^1J(^{187}Os-^{13}C)$ (± 1, in Hz)
$Os_3(CO)_{10}(Me_2C_2)$ (**3**)	210.3	a	45
	178.1	b	115
	174.5	c	–
	180.0	d	127
	174.1	e	–
	173.0	f	107
$Os_3(CO)_9P(OMe)_3(Me_2C_2)$ (**9**)	205.5	a	–
	175.3	b	90
	180.8	c, i	114
	181.9	d	88
	183.1	e	124
	172.8	f	124
	176.3, 174.2	g, h	116, 123
$Os_3(CO)_9PPh_3(Me_2C_2)$ (**10**)	178.6	e	117
	177.5	f	122
	175.5	h	125
	178.5	b	101

It can be seen from Fig. 3 that as the sample is warmed from 183 to 203 K, the resonances due to the carbonyl ligands labelled as d, e, f start to broaden, whereas the resonances due to the carbonyl ligands labelled as a, b, c remain sharp. This suggests that the activation barrier to localized scrambling within the set of carbonyl ligands associated with the osmium atom to which the alkyne forms σ-bonds is lower than that for the carbonyl ligands associated with the osmium atoms with which the alkyne forms a π-bond, and is consistent with the mechanism reported previously for the methyl- and ethyl-acetylene derivatives [16]. However, this result is in contrast with the dynamic behavior of the carbonyl ligands observed for the complex $Fe_3(CO)_8(Ph_2C_2)_2$ [23]. Here, the carbonyl ligands associated with the iron atom with highest coordination number (σ-bonded to alkynic carbons) remain rigid whereas the carbonyl ligands associated with an iron atom with low coordination number (π-bonded to alkynic carbons) are non-rigid at room temperature. In this case, a simple argument based on steric effects arising from the high coordination number about the iron atom has been put forward by Milone and coworkers [22] to explain the rigidity of carbonyl ligands. This does certainly not apply in the case of **3**.

At 243 K, the resonances b, c remain sharp, whereas the resonance due to bridging carbonyl ligand a disappears and an average broad signal (due to carbonyl ligands a, d, e, f) centered at δ 177 appears, indicating that there is a fluxional process involving an exchange of the carbonyl ligands (a, d, e, f) between these two osmium atoms. On further warming to 273 K, the remaining resonances b, c also broaden, and finally, at 353 K, the spectrum exhibits an average signal due to the carbonyl ligands, indicating that a second fluxional process involves intramolecular scrambling of all the ten carbonyl ligands. Attempts have been made to measure $^1J(Os-C)$ at higher temperatures, but even at 353 K the resonance is not sharp

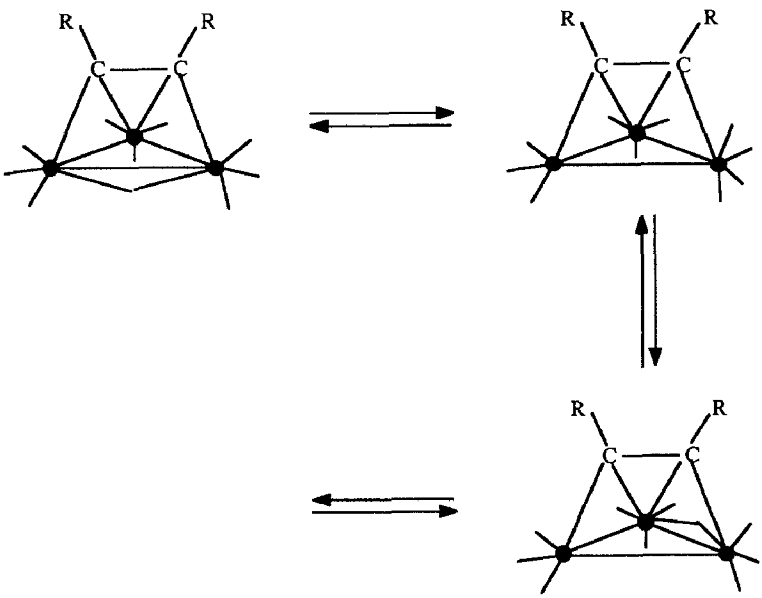

Fig. 4. Proposed mechanism for CO exchange in the complex $Os_3(CO)_{10}(R_2C_2)$.

enough to observe ^{187}Os satellites, and further warming results in the partial decomposition of the sample.

A possible mechanism (Fig. 4) shows an intramolecular exchange of carbonyl ligands mechanism involves the interconversion of bridged and non-bridged intermediates, and has been discussed previously [16]. The non-bridged form has been crystallographically characterized in the solid state for the diphenylacetylene derivative, $Os_3(CO)_{10}(Ph_2C_2)$ [10], although incipient bridging carbonyl ligands are present. The bridged form has been proposed on the basis of spectroscopic data for the complexes $Os_3(CO)_{10}(R_2C_2)$ (R = Et or Me) [19].

^{13}C NMR study of $Os_3(CO)_9P(OMe)_3(R_2C_2)$ (R = Et or Me)

The $^{13}C\{^1H\}$ NMR spectrum of $Os_3(CO)_9P(OMe)_3(Et_2C_2)$ displays two singlet resonances at δ 129 and 128.2 assigned to two inequivalent alkynic carbons. The appearance of two distinct resonances due to alkynic carbons once again indicates that the diethylacetylene moiety in this complex is rigid in solution at room temperature. A weak, broad resonance is also visible in the spectrum at δ 180.7 due to the carbonyl ligands. This indicates that the carbonyl ligands are fluxional. The dynamic behavior of the carbonyl ligands has been examined in complete detail by ^{13}C NMR studies of the complex $Os_3(CO)_9P(OMe)_3(Me_2C_2)$ (**9**). An enriched (^{13}CO) sample of **9** was used. The spectrum of **9** at 293 K shows resonances at δ 200, 180 and 177.4 due to the carbonyl ligands.

The ^{13}C NMR spectrum of **9** recorded at various temperatures is shown in Fig. 5. The mobility of the carbonyl ligands can be suppressed by cooling the sample to 198 K, where the NMR spectrum exhibits eight singlet resonances with relative intensities in the ratio of 1/1/1/2/1/1/1/1. No P–C coupling is seen at this temperature probably due to poor resolution. The low-field resonance at δ 205.5 is straightforwardly assigned to a bridging carbonyl ligand (labelled as a). The resonance at δ

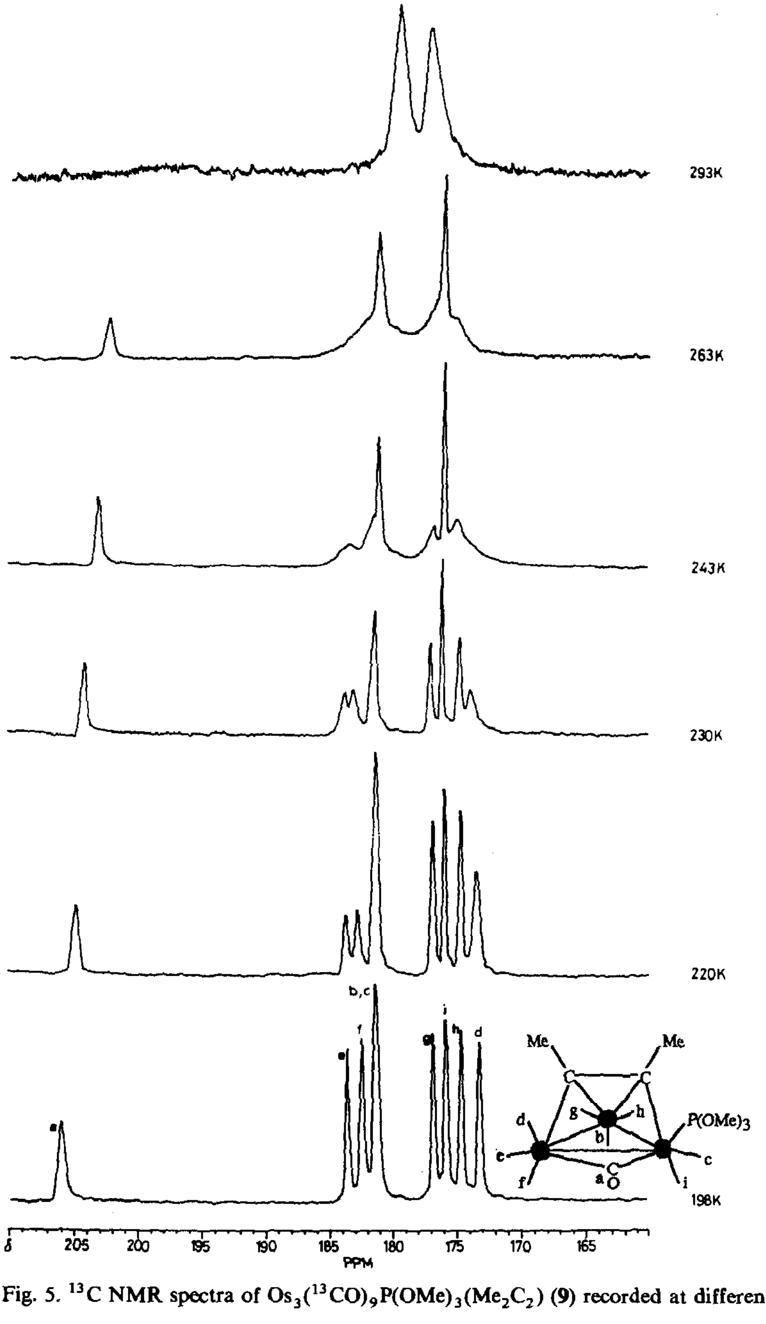

Fig. 5. ^{13}C NMR spectra of $Os_3(^{13}CO)_9P(OMe)_3(Me_2C_2)$ (9) recorded at different temperatures.

180.8 with intensity 2 is assigned to the carbonyl ligands labelled as c and i. The appearance of a single resonance due to these two inequivalent carbonyl ligands suggests that they are still fluxional. No change in the spectrum was noticed even on further cooling to 183 K. The various nuclear spin–spin coupling constants ($^1J(^{187}Os-^{13}C)$) are recorded in Table 4, together with their assignments. For axial carbonyl ligands $^1J(^{187}Os-^{13}C)$ is typically ca. 90 Hz, whereas for the equatorial carbonyl ligands it is ca. 120 Hz, comparable to the coupling constants reported for both axial and equatorial carbonyl ligands in $Os_3(CO)_{12}$ [21].

As the temperature is raised from 198 to 220 K, the resonances due to carbonyl ligands d, e, f start to broaden, suggesting that a localised scrambling of the carbonyl ligands at an osmium atom is taking place. Further warming to 243 K results in the broadening of two more resonances labelled as g, h whereas the resonances due to carbonyl ligands a, b stay sharp. Although the exact nature of the fluxional process is not completely understood, it is clear that no internuclear exchange of carbonyl ligands is taking place at 243 K or even up to 263 K as the resonance due to bridging carbonyl ligand labelled as a remains distinct. On further warming to 293 K, the resonance due to bridging carbonyl ligand disappears, and at

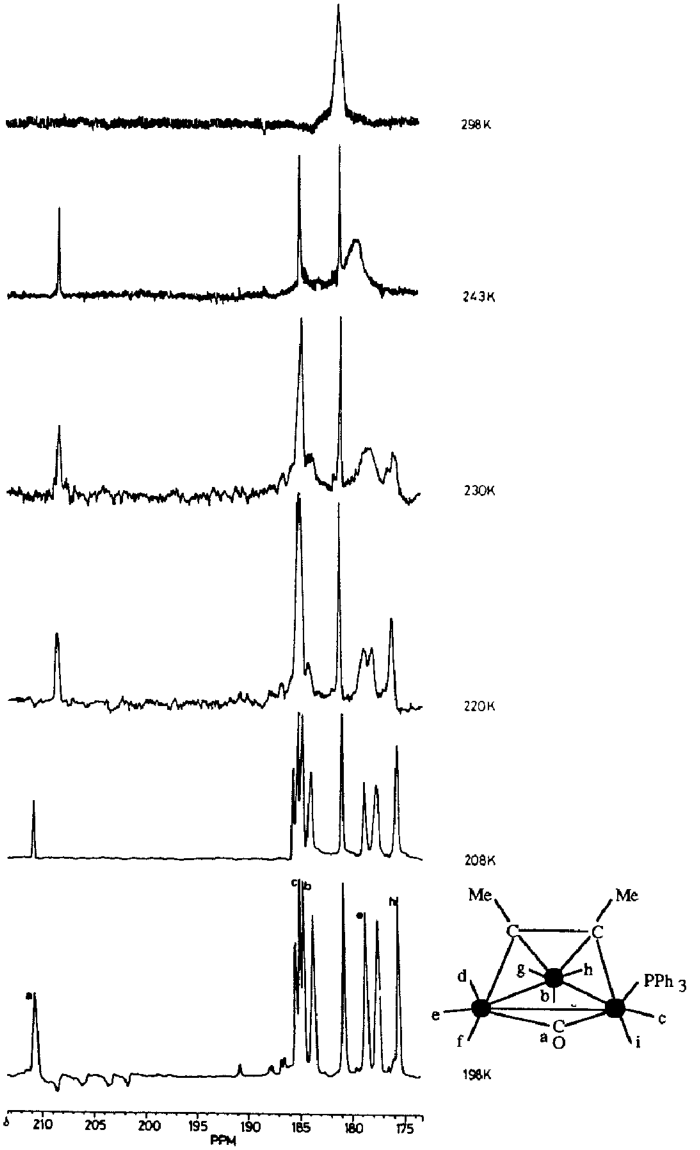

Fig. 6. ^{13}C NMR spectra of $Os_3(CO)_9PPh_3(Me_2C_2)$ (**10**) recorded at different temperatures.

353 K an average broad signal due to carbonyl ligands is visible at δ 181.0, indicative of total scrambling of the carbonyl ligands over the trimetallic framework. This means that the carbonyl ligands have access to each osmium atom and the exchange possibly occurs via an intramolecular mechanism involving bridged-non-bridged intermediates. The non-bridged form is crystallographically characterised in the solid state for the diphenylacetylene derivative **7**, although the incipient bridging carbonyls do suggest a possible pathway for the fluxional process. The bridged form has been proposed on the basis of spectroscopic data for the complexes $Os_3(CO)_9P(OMe)_3(Me_2C_2)$ (**9**), and this is entirely consistent with the conclusion reached by Aime et al. [16]. Attempts were made to measure $^1J(^{187}Os-^{13}C)$ at higher temperature, but even at ca. 363 K, the resonance was not sharp enough for observation of ^{187}Os satellites.

^{13}C NMR study of $Os_3(CO)_9PPh_3(Me_2C_2)$ (10)

The fluxional behavior of the carbonyl ligands in the complex $Os_3(^{13}CO)_9PPh_3(Me_2C_2)$ (**10**) in solution was examined by variable temperature ^{13}C NMR studies. The ^{13}C NMR spectrum of this complex recorded at various temperatures is shown in Fig. 6. The limiting spectrum, consistent with the structure of **10**, was obtained at 198 K. Nine resonances due to the carbonyl ligands are visible at this temperature. The low-field resonance at δ 210.6 is straightforwardly assigned to a bridging carbonyl ligand, and is split by the phosphorus atom of the $^{31}PPh_3$ ligand ($^2J(^{31}P-^{13}C)$ 8.8 Hz), indicating that the triphenylphosphine ligand is bonded *trans* to the bridging carbonyl ligand. The resonance at δ 185.4 assigned to CO^i also shows coupling to the $^{31}PPh_3$ ligand ($^2J(^{31}P-^{13}C)$ 7.5 Hz). Further assignments of the resonances were not possible, and the assignments shown in Fig. 6 are arbitrary. The $^1J(^{187}Os-^{13}C)$ for the carbonyl ligands labelled as e, f and h are recorded in Table 4. It was not possible to measure $^1J(^{187}Os-^{13}C)$ for other resonances owing to the proximity of the chemical shifts and broadening of the resonances.

The exact nature of the fluxional process is difficult to understand, but the data are entirely consistent with the interpretation proposed by Aime et al. [16]. A three stage exchange process occurs: (i) upon going from 198 to 208 K three resonances labelled as d, e, f begins to broaden, indicating that the first fluxional process involves localised scrambling of carbonyl ligands, (ii) At 243 K the resonances due to bridging carbonyl ligand a remains sharp, suggesting that no internuclear exchange of carbonyl ligands is taking place, (iii) At 298 K and average signal due to all the nine carbonyl ligands appears at δ 181.3, suggesting that all the carbonyl ligands are fluxional, and interact with all the three distinct osmium atoms via an intramolecular exchange process.

Experimental

Unless otherwise stated, manipulations of starting materials and products were carried out under nitrogen. The osmium complexes, $Os_3(CO)_{10}(R_2C_2)$ [17,24] (R = Ph, Et or Me), $Os_3(CO)_{12-n}(NCMe)_n$ ($n = 1$ or 2) [25] were prepared by published methods. The ^{13}CO-enriched compounds were obtained from ^{13}CO-enriched $Os_3(CO)_{12}$ (ca. 40% ^{13}C). The ^{13}CO-enriched $Os_3(CO)_{12}$ was prepared by stirring $Os_3(CO)_{10}(NCMe)_2$ with ^{13}CO at room temperature for several hours [26]. The Me_3NO, obtained commercially, was sublimed before use.

Proton and ^{31}P NMR spectral data were obtained on Bruker WM250 at 20 °C using deuteriated solvent as internal lock and reference (^{1}H: $SiMe_4$, $\delta = 0$; ^{31}P: 1% $P(OMe)_3$ in C_6D_6; $\delta = 0$, downfield positive). Variable temperature ^{13}C NMR spectra were recorded on Bruker WM400 using CD_2Cl_2 as internal lock and reference, and the ^{187}Os satellites in the limiting ^{13}C NMR spectra of $Os_3(CO)_9L(Me_2C_2)$ (L = CO, $P(OMe)_3$, PPh_3) were recorded by a previously described procedure [22].

Preparation of $Os_3(CO)_9(NCMe)(R_2C_2)$. The compound $Os_3(CO)_{10}(R_2C_2)$ (**1**: R = Ph; **2**: R = Et or **3**: R = Me) (30 mg) was dissolved in CH_2Cl_2 (30 cm^3) and MeCN (1.0 cm^3). A solution of Me_3NO (1.1 equiv.) in CH_2Cl_2 was added dropwise to the stirred suspension at −78 °C during 0.5 h. The mixture was gradually warmed to room temperature and then stirred for about 0.5 h. It was then filtered through silica to remove any unchanged amine-oxide, and the solvent was then removed on a rotary evaporator. The product, formulated as $Os_3(CO)_9(NCMe)(R_2C_2)$ (**4**: R = Ph, **5**: R = Et or **6**: R = Me), was used in subsequent reactions without any further purification.

Reaction of $Os_3(CO)_9(NCMe)(R_2C_2)$ with CO. The cluster $Os_3(CO)_9(NCMe)(R_2C_2)$ (**4**: R = Ph, **5**: R = Et or **6**: R = Me) was dissolved in CH_2Cl_2 and CO (1 atm) was bubbled through for 0.5 h. The solvent was removed under pressure. Purification by thin layer chromatography gave $Os_3(CO)_{10}(R_2C_2)$ (**1**: R = Ph, **2**: R = Et or **3**: R = Me) as the major product.

*Reaction of $Os_3(CO)_9(NCMe)(Ph_2C_2)$ (**4**) with H_2.* H_2 gas (1 atm) was bubbled through a CH_2Cl_2 solution of $Os_3(CO)_9(NCMe)(Ph_2C_2)$ (**4**) at room temperature for 0.5 h. Work up by TLC afforded $H_2Os_3(CO)_9(Ph_2C_2)$ in 30% yield.

*Reaction of $Os_3(CO)_9(NCMe)(Ph_2C_2)$ (**4**) with Ph_2C_2.* To a CH_2Cl_2 solution of $Os_3(CO)_9(NCMe)(Ph_2C_2)$ (**4**) was added an excess of Ph_2C_2 (1.5 equiv). The mixture was stirred for 2 h, during which the colour changed from yellowish orange to violet. Purification by TLC (40% CH_2Cl_2 in hexane)afforded the known violet cluster $Os_3(CO)_9(Ph_2C_2)_2$ in 85% yield.

*Reaction of $Os_3(CO)_9(NCMe)(Ph_2C_2)$ (**4**) with Me_2C_2.* The cluster $Os_3(CO)_9(NCMe)(Ph_2C_2)$ (**4**) (25 mg) was stirred with four fold excess of Me_2C_2 in a sealed Carius tube at room temperature for 1 h. Removal of solvent, followed by thin layer chromatography (30% CH_2Cl_2 in hexane) afforded a violet cluster, shown to be $Os_3(CO)_9(Ph_2C_2)(Me_2C_2)$ in 80–85% yield.

Reaction of $Os_3(CO)_9(NCMe)(R_2C_2)$ with $P(OMe)_3$. The cluster $Os_3(CO)_9(NCMe)(R_2C_2)$ (**4**: R = Ph, or **6**: R = Me) (25 mg) was stirred with two drops of $P(OMe)_3$ in CH_2Cl_2 at room temperature for 15 min. The solvent and the excess of $P(OMe)_3$ were removed in a fast stream of N_2. Thin layer chromatography (50% CH_2Cl_2 in hexane) of the residue gave $Os_3(CO)_9P(OMe)_3(R_2C_2)$ (**7**: R = Ph, or **9**: R = Me) in 75–80% yield.

Reaction of $Os_3(CO)_9(NCMe)(R_2C_2)$ with PPh_3. Triphenylphosphine (1.1 equiv.) was added to a CH_2Cl_2 solution of $Os_3(CO)_9(NCMe)(R_2C_2)$ (**5**: R = Et, or **6**: R = Me) and the mixture was stirred for 0.5 h. Removal of solvent followed by thin layer chromatography gave $Os_3(CO)_9(PPh_3)(R_2C_2)$ (**8**: R = Et, or **10**: R = Me) in 70% yield.

Crystal structure determination of $Os_3(CO)_9P(OMe)_3(Ph_2C_2)$. Suitable single crystals were obtained as orange multifaceted blocks from CH_2Cl_2/hexane solution. A crystal with dimensions (distance from face to centre): 0.112 $(010, 0\bar{1}0)$ ×

0.209 (001, 00$\bar{1}$) × 0.072 (10$\bar{1}$, $\bar{1}$01) × 0.093 (11$\bar{1}$, $\bar{1}$11) mm was mounted on a glass fibre with epoxy resin.

Crystal data. $C_{26}H_{19}O_{12}POs_3$, M 1124.98, Monoclinic, a 11.130(2), b 15.207(1), c 18.445(2) Å, β 106.26(1)°, V 2997(1) Å^3 (by least-squares refinement on diffractometer angles from 60 automatically centred reflections in the range $20 < 2\theta < 25$°, λ 0.71069 Å), space group $P2_1/n$ (alt. setting $P2_1/c$, No. 14), $Z = 4$, D_c 2.492

Table 5

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Os(1)	8140(1)	3096(1)	4119(1)	35(1)
Os(2)	7759(1)	3486(1)	5569(1)	38(1)
Os(3)	5815(1)	2893(1)	4438(1)	37(1)
P(1)	9101(4)	2349(3)	3341(2)	48(1)
O(1)	9852(11)	1569(8)	3750(6)	81(5)
C(1)	10536(22)	897(15)	3473(14)	115(7)
O(2)	8108(11)	2030(8)	2592(6)	81(5)
C(2)	8289(22)	1697(15)	1928(12)	106(7)
O(3)	9924(15)	2827(10)	2913(10)	120(8)
C(3)	11073(34)	3182(24)	3335(21)	353(20)
C(11)	8710(15)	4302(10)	4040(8)	56(4)
O(11)	9077(14)	4964(7)	4025(8)	102(7)
C(12)	6735(14)	3300(9)	3211(8)	48(4)
O(12)	6070(10)	3464(9)	2647(6)	82(5)
C(13)	9652(14)	2824(9)	4968(8)	45(3)
O(13)	10587(10)	2631(8)	5339(5)	73(5)
C(21)	6873(15)	3538(10)	6341(9)	56(4)
O(21)	6378(12)	3528(8)	6778(7)	38(3)
C(22)	7674(16)	4748(12)	5416(10)	68(5)
O(22)	7566(15)	5469(7)	5264(9)	112(7)
C(23)	9318(15)	3442(9)	6307(9)	52(4)
O(23)	10250(11)	3422(8)	6781(6)	75(5)
C(31)	4683(15)	2701(10)	5005(9)	58(4)
O(31)	3993(13)	2582(9)	5362(7)	97(7)
C(32)	4702(13)	2336(8)	3574(8)	41(3)
O(32)	3952(10)	2059(8)	3077(6)	72(5)
C(33)	5237(15)	4081(11)	4224(9)	62(4)
O(33)	4967(13)	4791(7)	4063(7)	93(6)
C(10)	7388(11)	1964(8)	4550(7)	33(4)
C(20)	7399(12)	2161(8)	5311(7)	35(5)
C(102)	6721(8)	831(5)	3512(4)	48(3)
C(103)	6820	−7	3226	70(5)
C(104)	7586	−637	3679	80(5)
C(105)	8253	−430	4419	79(5)
C(106)	8153	408	4706	58(4)
C(101)	7388	1038	4252	36(3)
C(202)	6099(7)	913(6)	5647(4)	57(4)
C(203)	5952	271	6156	62(4)
C(204)	6837	191	6858	58(4)
C(205)	7867	754	7051	50(4)
C(206)	8013	1397	6543	51(4)
C(201)	7129	1477	5841	39(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

g cm^{-3}, $F(000) = 2056$, graphite monochromated Mo-K_α radiation, μ(Mo-K_α) 127.80 cm^{-1}.

Data collection and processing. Stoe–Siemens four-circle diffractometer, 24 step ω/θ scan, step width 0.04°, scan speed 0.5–2.0 s per step; on-line profile fitting. 8466 Reflections measured ($5.0 \leq 2\theta \leq 45.0°$, $\pm h$, $\pm k$, $-l$), numerical absorption correction applied (min., max. transmission factors = 0.074, 0.179), giving 3905 unique data ($R_{int} = 0.050$), and 3316 observed data with $F > 4\sigma(F)$. Three standard reflections showed no significant variation during data collection.

Structure solution and refinement. Centrosymmetric direct methods (Os atoms) followed by Fourier-difference syntheses for the remaining non-hydrogen atoms. Blocked-cascade least-squares with Os, P, O and alkyne C atoms anisotropic. Phenyl rings were refined as regular hexagons (C–C, 1.395 Å; C–C–C, 120.0°). Phenyl- and methyl-H atoms were placed in idealised positions and allowed to ride 1.08 Å from the relevant C atom; methyl groups were treated as rigid groups. Each type of H atom was assigned a common isotropic temperature factor. The weighting scheme $w = 3.098/[\sigma^2F + 0.0008F^2]$ gave satisfactory agreement analyses. The final converged residuals were $R = 0.042$ and $R_w = 0.044$ for 243 refined parameters. A final difference map showed no significant regions of electron density except for ripples of 1.1 eÅ^{-3} close to the Os atom positions. Complex neutral atom scattering factors were employed [27], and all computations were performed on the University of Cambridge IBM3084Q computer using SHELX76 [28]. The final atomic fractional coordinates are presented in Table 5. Details of thermal parameters, complete lists of bond parameters, and structure factor tables may be obtained from the authors.

Acknowledgements

We thank the Nehru Trust (India), the Cambridge Commonwealth Trust, and the Committee of Vice-Chancellors and Principals for the financial support (to RK), the Royal Commission for the Exhibition of 1851 and the University Grants Committee (New Zealand) for the award of a scholarship (to MAG).

References

1 E. Sappa, A. Tiripicchio and P. Braunstein, Chem. Rev., 83 (1983) 203.
2 P.R. Raithby and M.J. Rosales, Adv. Inorg. Chem. Radiochem., 29 (1985) 169.
3 E.L. Muetterties. T.N. Rhodin, E. Band, C.F. Brucker and W.R. Pretzer, Chem. Rev., 79 (1979) 91.
4 V. Busetti, G. Granozzi, S. Aime, R. Gobetto and D. Osella, Organometallics, 3 (1984) 1510.
5 D. Boccardo, M. Botta, R. Gobetto, D. Osella, A. Tiripicchio and M. Tiripicchio-Camelline, J. Chem. Soc., Dalton Trans., (1988) 1249.
6 S. Aime, R. Bertoncello, V. Busetti, R. Gobetto, G. Granozzi and D. Osella, Inorg. Chem., 25 (1986) 4004.
7 B.E.R. Schilling and R. Hoffmann, J. Am. Chem. Soc., 101 (1979) 3456.
8 A.J. Deeming, S. Hasso and M. Underhill, J. Chem. Soc., Dalton Trans., (1975) 1614.
9 J. Evans and S. McNulty, J. Chem. Soc., Dalton Trans., (1981) 2017 and ref. therein.
10 C.G. Pierpont, Inorg. Chem., 16 (1977) 636.
11 J.F. Blount, L.F. Dahl, C. Hoogzard and W.J. Hübel, J. Am. Chem. Soc., 88 (1966) 292.
12 J.A. Clucas, P.A. Dolby, M.M. Harding and A.K. Smith, J. Chem. Soc., Chem. Commun., (1987) 1829.
13 A.J. Deeming, J. Organomet. Chem., 150 (1978) 123.
14 J.R. Shapley, S.I. Richter, M. Tachikawa and J.B. Keister, J. Organomet. Chem., 94 (1975) C43.
15 F.W.B. Einstein, K.G. Tyers, A.S. Tracey and D. Sutton, Inorg. Chem., 25 (1986) 1631.

16 E. Rosenberg, J. Bracker-Novak, R.W. Gelbert, S. Aime, R. Gobetto and D. Osella, J. Organomet. Chem., 365 (1989) 163.

17 M. Tachikawa and J.R. Shapley, J. Organomet. Chem., 124 (1977) C19.

18 G. Ferraris and G.J. Gervasio, Chem. Soc., Dalton Trans., (1974) 1813.

19 M. Tachikawa, J.R. Shapley and C.G. Pierpont, J. Am. Chem. Soc., 97 (1975) 7172.

20 R.A. Kamarudin, Ph.D. Thesis, University of Cambridge, 1987.

21 A.A. Koridze, O.A. Kizas, N.M. Astakhova, P.V. Petrovskii and Y.K. Grishin, J. Chem. Soc., Chem. Commun., (1981) 853.

22 M.A. Gallop, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Chem. Commun., (1987) 1831.

23 S. Aime, L. Milone and E. Sappa, Inorg. Chim. Acta, 16 (1976) L7.

24 B.F.G. Johnson, R. Khattar, J. Lewis, P.R. Raithby and D.N. Smit, J. Chem. Soc., Dalton Trans., (1988) 1421.

25 S.R. Drake and R. Khattar, Organomet. Syntheses, 4 (1988) 234.

26 S.R. Drake, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., (1988) 1517.

27 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, Vol. 4.

28 SHELX76, Crystal Structure Solving Package, G.M. Sheldrick, Cambridge, 1976.