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Reactions of the unsaturated alkyne cluster $[Os_3(CO)_7\{\mu_3\text{-}\eta^2(\perp)\text{-}PhC_2Ph\}(dppm)]$ with P-donors; crystal structures of $[Os_3(CO)_6(PhC_2Ph)(dppm)\{P(OMe)_3\}]$ and two isomers of $[Os_3(CO)_7(PhC_2Ph)(dppm)(PBu_3)]$ (dppm = $Ph_2PCH_2PPh_2$)

Rachel A. Harding and Anthony K. Smith *

Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

Treatment of the unsaturated cluster $[Os_3(CO)_7(PhC_2Ph)(dppm)]$ **1** (dppm = $Ph_2PCH_2PPh_2$) with P-donors gave the saturated monoadducts $[Os_3(CO)_7(PhC_2Ph)(dppm)L]$ [L = PBu_3 **2**, PPh_3 **3**, PMe_2Ph **4** or $P(OMe)_3$ **5**]. Spectroscopic studies have established that these adducts exist in three isomeric forms the ratio of which depends on the polarity of the solvent used in the reaction. X-Ray crystallographic determinations of two isomers of the PBu_3 adduct, **2a** and **2c**, showed the phosphine to be co-ordinated to different metal centres in the two isomers. The $P(OMe)_3$ adducts **5b** and **5c** underwent a facile decarbonylation reaction to give the unsaturated cluster $[Os_3(CO)_6(PhC_2Ph)(dppm)\{P(OMe)_3\}]$ **6**, which has been structurally characterised by X-ray crystallography. Attempts to decarbonylate the monoadducts **2**–**4** have been unsuccessful.

In recent years the structural and bonding aspects of trinuclear metal alkyne clusters have been extensively studied.[1] The mode of co-ordination of disubstituted alkynes to the trimetallic framework has two principal forms and is known to be strongly dependent on the number of valence electrons, the substituents on the alkyne and the back-donation ability of the metal to the alkyne. The principal modes are μ_3-$\eta^2(\perp)$, observed in unsaturated 46-electron clusters, and the more common μ_3-$\eta^2(||)$ mode observed in 48-electron clusters (Scheme 1).

μ_3-$\eta^2(\perp)$ μ_3-$\eta^2(||)$

Scheme 1

The red, unsaturated cluster $[Os_3(CO)_7\{\mu_3\text{-}\eta^2(\perp)\text{-}PhC_2Ph\}(dppm)]$ **1** (dppm = $Ph_2PCH_2PPh_2$) has been synthesised in good yield by the addition of an excess of diphenylacetylene to the unsaturated cluster $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$.[2] We have previously reported the addition of CO and H_2 to complex **1** and have shown that the saturated, 48-electron products contain the alkyne co-ordinated in a μ_3-$\eta^2(||)$ mode.[2,3] Two-electron electrochemical reduction of **1** also causes the same change in co-ordination mode of the alkyne ligand.[3]

We now report on the reactions of the alkyne complex **1** with tertiary phosphines and phosphites together with the decarbonylation reaction of a monophosphite adduct to give a new co-ordinatively unsaturated triosmium cluster.

Results and Discussion

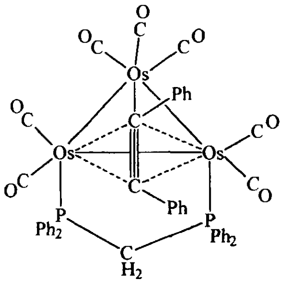
Treatment of a toluene solution of the red, unsaturated cluster **1**, with 1 equivalent of the P-donor L [L = PBu_3, PPh_3, PMe_2Ph or $P(OMe)_3$] results in the formation of the monoadducts $[Os_3(CO)_7(PhC_2Ph)(dppm)L]$ [L = PBu_3 **2**, PPh_3 **3**, PMe_2Ph **4** or $P(OMe)_3$ **5**]. The rate of reaction was dependent on the steric requirements of the ligand L, as previously reported for the addition of phosphines to the unsaturated complex $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$.[4] Low-temperature ^{31}P NMR studies of the reaction between complex **1** and PBu_3 revealed the presence of three products (see Table 1). The spectra show three singlets due to co-ordinated PBu_3 and three pairs of doublets of doublets, with different phosphorus–phosphorus couplings, due to the dppm ligand. This pattern of signals was characteristic of all adducts **2**–**5**. In all cases, attempts to separate the isomers by TLC were unsuccessful. However, two crystalline forms of the adduct **2** were obtained, one orange (**2a**) and one red (**2c**). The crystal structures of these isomers were determined, although that of **2c** could not be satisfactorily refined (R = 0.113) due to crystal decomposition during data collection. Nevertheless, only the carbon atoms of the PBu_3 ligand were not located so that sufficient structural detail was obtained to show that the PBu_3 has added to the Os atom not co-ordinated to the dppm ligand and that the alkyne has adopted a μ_3-$\eta^2(||)$ co-ordination mode with σ bonds to the Os atom bonded to PBu_3 and one of the Os atoms bonded to the μ-dppm ligand (Fig. 1). All the phosphorus ligands occupy equatorial co-ordination sites. The structure of isomer **2a** is shown in Fig. 2 and selected bond lengths and angles are given in Table 2. In this isomer the PBu_3 ligand has added to an osmium atom which is also co-ordinated to a phosphorus atom of the μ-dppm ligand, the μ-dppm ligand adopts axial co-ordination sites, and the $\mu_3,\eta^2(||)$ alkyne is σ bonded to the Os atoms [Os(1) and Os(2)] bridged by the dppm ligand. There is also a semibridging CO ligand [Os(1)–C(2)–O(2) 159(1)°]. This contrasts with the symmetrically bridging CO ligand found in the analogous complexes $[Os_3(CO)_8\{\mu_3\text{-}\eta^2(||)\text{-}RC{\equiv}CR\}(dppm)]$ (R = Me or CF_3),[3] and with the structure of $[Os_3(CO)_{10}(PhC{\equiv}CPh)]$ in which there are two asymmetrically bridging CO ligands.[5] It is suggested that the presence of the μ-CO ligand enforces axial co-ordination of the dppm ligand. The presence of the PBu_3 ligand also leads to some asymmetry in the co-ordination of the alkyne ligand [Os(1)–C(33) 2.14(1), Os(2)–C(34) 2.08(1) Å], with the longer osmium–carbon bond involving the osmium atom co-ordinated to two phosphorus atoms. The Os(1)–Os(2) bond length [2.885(1) Å] is also significantly longer than those found for the equivalent Os–Os bonds in $[Os_3(CO)_8(RC{\equiv}CR)(dppm)]$ [R = Me, 2.810(1); R = CF_3, 2.818(2) Å].[3]

Crystals of the third isomer, **2b**, were not obtained. However, in attempting to grow crystals from an isomeric mixture of

Table 1 The NMR data for the products of the reaction of $[Os_3(CO)_7(PhC_2Ph)(dppm)]$ **1** with L

L	Compound	$^{31}P-\{^1H\}^a$ dppm	L
	1	3.77 (s)	
PBu_3	**2a**	0.35 [d, J(PP) 112], −16.0 (d)	−26.0 (s)
	2b	−17.6 [d, J(PP) 55], −20.4 (d)	−17.9 (s)
	2c	−29.3 [d, J(PP) 32], −37.1 (d)	−14.2 (s)
PPh_3	**3a**	2.4 [d, J(PP) 80], −9.15 (d)	−5.8 (s)
	3b	−17.3 [d, J(PP) 56], −24.8 (d)	13.6 (s)
	3c	−28.8 [d, J(PP) 31], −40.5 (d)	15.8 (s)
PMe_2Ph	**4a**	−1.65 [d, J(PP) 113], −11.5 (d)	−33.0 (s)
	4b	−18.2 [d, J(PP) 54], −20.6 (d)	−31.2 (s)
	4c	−27.05 [d, J(PP) 32], −38.6 [dd, J(PP) 32 and 8.5][b]	−27.7 (br s)
$P(OMe)_3$	**5a**	−2.1 [d, J(PP) 113], −13.2 (d)	107.7 (s)
	5b	−19.3 [d, J(PP) 53], −22.8 (d)	103.5 (s)
	5c	−28.5 [d, J(PP) 31], −41.2 [dd, J(PP) 31 and 13][b]	111.2 (br s)
$P(OMe)_3$	**6**	3.47 (s)	97.0 (s)

[a] Chemical shifts relative to 85% H_3PO_4 (δ 0); coupling constants in Hz. [b] Small coupling of one P atom of dppm with the P atom of ligand L observed; this was not resolved on the resonance of L which only showed some broadening.



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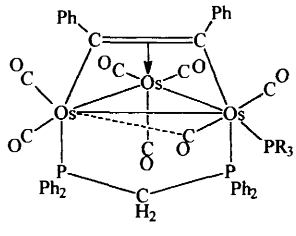
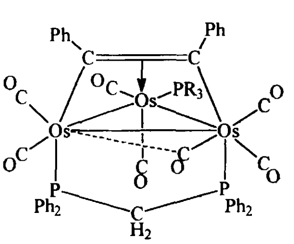
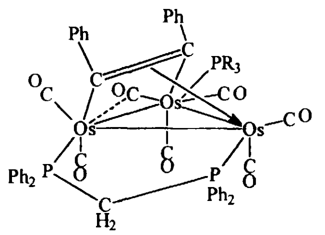


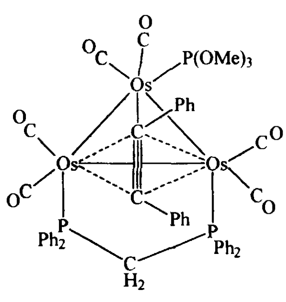
2a R = Bu
3a R = Ph
4a $R_3 = Me_2Ph$
5a R = OMe



2b R = Bu
3b R = Ph
4b $R_3 = Me_2Ph$
5b R = OMe



2c R = Bu
3c R = Ph
4c $R_3 = Me_2Ph$
5c R = OMe



6

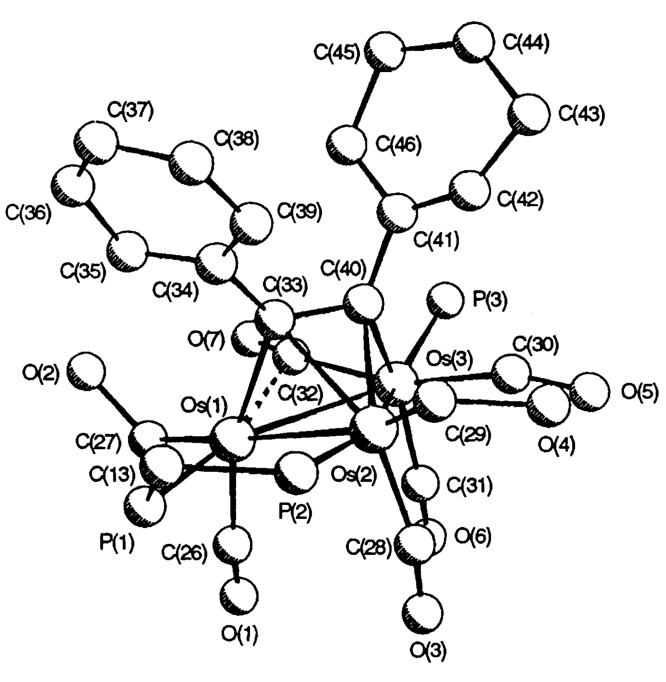


Fig. 1 Structure of $[Os_3(CO)_7(PhC_2Ph)(dppm)(PBu_3)]$ **2c**

the trimethyl phosphite derivatives, **5**, the dichloromethane–heptane solution gradually changed from orange to red, and deep red crystals were eventually obtained. A crystal structure determination showed that the 46-electron cluster $[Os_3(CO)_6\{\mu_3,\eta^2(\perp)\text{-}PhC{\equiv}CPh\}(dppm)\{P(OMe)_3\}]$ **6** had been formed. The molecular structure of **6** is shown in Fig. 3, and selected bond lengths and angles are given in Table 3. The structure is similar to that of the starting cluster $[Os_3(CO)_7(PhC{\equiv}CPh)(dppm)]$ **1**, with the $P(OMe)_3$ co-ordinated at an equatorial site on the unique osmium atom Os(3). The unsaturated, 46-electron cluster has two characteristically short osmium–osmium bonds [Os(1)–Os(3) 2.697(2), Os(2)–Os(3) 2.684(2) Å], as was found in the parent cluster, **1**,[2] indicating that the unsaturation is delocalised. The spectroscopic data for **6** (Table 1) show that the phosphorus atoms of the dppm ligand are equivalent and show no coupling to the $P(OMe)_3$ ligand. This suggests that in solution there is rapid trigonal rotation of the $P(OMe)_3$ ligand and the two carbonyl ligands on Os(3). Since complex **6** is formed by addition of $P(OMe)_3$ to the alkyne cluster **1**, followed by decarbonylation, an attempt to recarbonylate **6** was made. It was found that **6** reacts readily with CO under ambient conditions [23 °C, 1 atm (*ca.* 10^5 Pa)] to generate an orange solution. The ^{31}P NMR spectrum of this solution showed that two isomers, **5b** and **5c**, were present, but significantly not **5a**. By refluxing the orange solution of **5b** and **5c** in toluene under nitrogen complex **6** was regenerated as the only product. This information enables us to assign structures

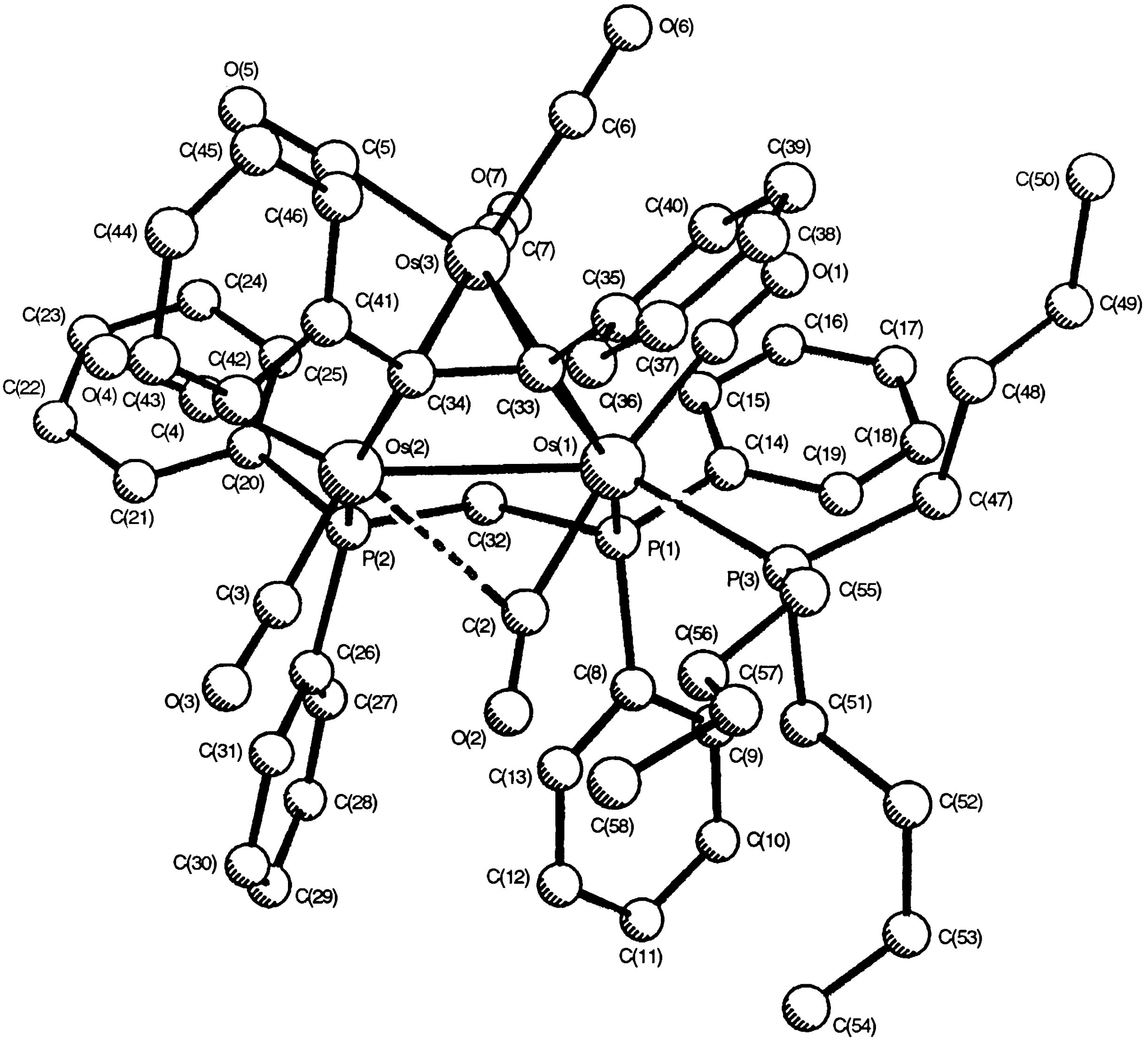


Fig. 2 Molecular structure of $[Os_3(CO)_7(PhC_2Ph)(dppm)(PBu_3)]$ **2a** with H atoms omitted

Table 2 Selected bond lengths (Å) and angles (°) for $[Os_3(CO)_7(PhC_2Ph)(dppm)(PBu_3)]$ **2a**

Os(1)–Os(2)	2.885(1)	Os(2)–C(4)	1.83(2)
Os(1)–Os(3)	2.783(1)	Os(2)–C(34)	2.08(1)
Os(2)–Os(3)	2.774(1)	Os(2) ··· C(2)	2.53(1)
Os(1)–P(1)	2.390(4)	Os(3)–C(5)	1.88(2)
Os(1)–P(3)	2.381(4)	Os(3)–C(6)	1.91(2)
Os(2)–P(2)	2.390(4)	Os(3)–C(7)	1.89(2)
Os(1)–C(1)	1.91(2)	Os(3)–C(33)	2.29(1)
Os(1)–C(2)	1.94(2)	Os(3)–C(34)	2.29(1)
Os(1)–C(33)	2.14(1)	C(33)–C(34)	1.38(2)
Os(2)–C(3)	1.82(2)		
Os(2)–Os(1)–Os(3)	58.57(3)	Os(3)–Os(2)–C(4)	93.3(5)
Os(1)–Os(2)–Os(3)	58.89(3)	Os(1)–Os(3)–C(6)	112.0(6)
Os(1)–Os(3)–Os(2)	62.54(3)	Os(1)–Os(3)–C(7)	97.8(5)
Os(2)–Os(1)–P(1)	92.1(1)	Os(2)–Os(3)–C(5)	93.2(6)
Os(3)–Os(1)–P(1)	106.6(1)	Os(2)–Os(3)–C(7)	103.7(5)
Os(2)–Os(1)–P(3)	141.5(1)	C(5)–Os(3)–C(6)	89.9(8)
Os(2)–Os(1)–C(2)	59.3(4)	C(5)–Os(3)–C(7)	93.0(7)
P(1)–Os(1)–P(3)	100.6(1)	C(6)–Os(3)–C(7)	91.8(8)
Os(3)–Os(1)–C(1)	72.1(5)	C(34)–C(33)–C(35)	123(1)
C(1)–Os(1)–P(3)	89.1(5)	C(33)–C(34)–C(41)	121(1)
C(2)–Os(1)–P(3)	83.9(4)	P(1)–C(32)–P(2)	116.7(7)
Os(1)–Os(2)–P(2)	93.5(1)	Os(1)–C(2)–O(2)	159(1)
Os(3)–Os(2)–P(2)	103.6(1)	Os(2)–C(2)–O(2)	121(1)
Os(1)–Os(2)–C(3)	115.6(5)	Os–C–O(mean)	176(2)
C(3)–Os(2)–C(4)	90.1(7)		

Table 3 Selected bond lengths (Å) and angles (°) for $[Os_3(CO)_6(PhC_2Ph)(dppm)\{P(OMe)_3\}]$ **6**

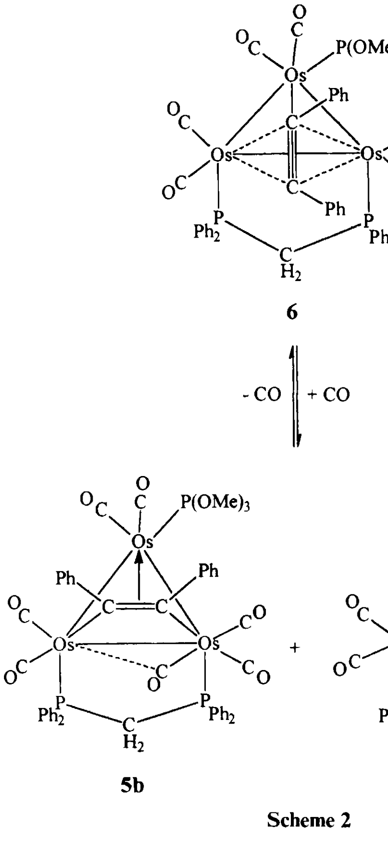
Os(1)–Os(2)	2.865(2)	Os(1)–C(32)	2.22(1)
Os(1)–Os(3)	2.697(2)	Os(1)–C(33)	2.11(1)
Os(2)–Os(3)	2.684(2)	Os(2)–C(32)	2.24(1)
Os(1)–P(1)	2.342(4)	Os(2)–C(33)	2.09(1)
Os(2)–P(2)	2.298(4)	Os(3)–C(32)	2.25(1)
Os(3)–P(3)	2.281(5)	C(32)–C(33)	1.39(2)
Os(2)–Os(1)–Os(3)	57.62(3)	Os(1)–Os(3)–P(3)	102.3(1)
Os(1)–Os(2)–Os(3)	58.05(6)	C(6)–Os(3)–P(3)	93.4(5)
Os(1)–Os(3)–Os(2)	64.33(4)	Os(2)–Os(3)–C(6)	94.4(5)
Os(3)–Os(1)–P(1)	93.1(1)	C(32)–C(33)–C(40)	126(1)
Os(1)–Os(2)–P(2)	91.5(1)	P(1)–C(19)–P(2)	115.0(8)
Os(3)–Os(2)–C(4)	125.7(5)		

to all three isomers of the phosphine and phosphite adducts and to correlate the NMR data with these structures. Attempts to decarbonylate compounds **2**–**4**, either by refluxing in toluene or by treatment with Me_3NO, were unsuccessful.

Since isomers **5b** and **5c** are obtained from complex **6** at room temperature by treatment with CO, it is reasonable to assume that these isomers will have the phosphite ligand on the unique osmium atom (*i.e.* one phosphorus atom is co-ordinated to each osmium atom in the cluster) since phosphite or phosphine ligands do not move between metal atoms except at much

Table 4 Crystal data, details of data collection and refinement

	Complex		
	2a	**2c**	**6**
Formula	$C_{58}H_{59}O_7Os_3P_3$	$C_{58}H_{59}O_7Os_3P_3$	$C_{48}H_{41}O_9Os_3P_3$
M	1531.6	1531.6	1425.4
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a/Å	12.669(4)	20.60(2)	17.72(2)
b/Å	20.178(6)	15.05(1)	13.53(1)
c/Å	11.567(3)	20.78(2)	20.00(2)
α/°	96.93(2)		
β/°	100.62(3)	113.49(6)	107.78(7)
γ/°	82.12(3)		
U/Å^3	2865(3)	5909(8)	4566(7)
Z	2	4	4
D_c/g cm^{-3}	1.773	1.722	2.073
$F(000)$	1472	2944	2696
Colour	Orange	Red	Red
Crystal size/mm	0.4 × 0.35 × 0.45	0.2 × 0.1 × 0.4	0.2 × 0.02 × 0.2
μ/cm^{-1}	67.73	65.67	84.95
Scan mode	ω–2θ	ω	ω–2θ
T/K	297	295	153
Total no. reflections	10 598	9594	7218
θ Range/°	0–50	0–50	0–50.5
No. of unique reflections	10 095	9273	6917
No. of observed reflections	6960 [$I > 4\sigma(I)$]	2661 [$I > 3\sigma(I)$]	4218 [$I > 4\sigma(I)$]
Absorption correction	DIFABS[7]	Empirical	DIFABS[7]
Crystal decay	None	73%	None
Weighting scheme, w	$1/\sigma^2(F)$	$1/\sigma^2(F)$	$1/\sigma^2(F)$
Final R	0.045	0.113	0.039
Final R'	0.068	0.105	0.045



Scheme 2

higher temperatures. Thus the reversible carbonylation of cluster **6** is suggested to proceed as shown in Scheme 2.

The structure of complex **5c** is thus analogous to that determined crystallographically for **2c**, while **5b** has the alkyne ligand parallel to the Os–Os bond bridged by the dppm ligand. These isomers are obtained by the addition of CO to Os(1) or Os(3) of complex **6**, respectively, or by the addition of $P(OMe)_3$ to the unique Os atom of **1**. The addition of $P(OMe)_3$ to Os(1) of complex **1** generates the cluster **5a**, analogous to **2a**. The ^{31}P NMR data for **5a** are unambiguously assigned as shown in Table 1, since these resonances are not observed on carbonylation of **6**. Furthermore, it has previously been observed that the chemical shifts of axially co-ordinated dppm phosphorus atoms occur at relatively low field.[3] The assignments of ^{31}P NMR resonances to **5b** and **5c** are less certain. However, the very different chemical environments of the two phosphorus atoms of the dppm ligand in **5c** compared to **5b**, suggests that the assignments are as given in Table 1 where there is a much larger chemical shift difference between the dppm phosphorus atoms in **5c** compared to **5b**. The similarities between the chemical shifts and coupling constants of the resonances for the dppm ligand in complexes **2**–**5** allow similar assignments to be made for each of the isomers **a**–**c**, with the exception of the triphenylphosphine isomer **3a**. In this case the J(PP) coupling constant (80 Hz) is significantly less than for the other **a** isomers (112–113 Hz). However, this could be ascribed to the steric effect of the bulky PPh_3 ligand (it has the largest cone angle of the phosphines or phosphites used in this study) which will affect the co-ordination geometry around the Os atom to which the PPh_3 and one end of the dppm ligand are co-ordinated and hence affect the coupling constant between the two phosphorus atoms of the dppm ligand.

It has been observed previously that the triiron–alkyne cluster $[Fe_3(\eta\text{-}C_5H_5)_2(CO)_5(F_3CC{\equiv}CCF_3)]$ exists in solution as symmetrical and asymmetrical isomers whose proportions are dependent on solvent polarity.[6] It was therefore of interest to determine the influence of the solvent on the reaction of cluster **1** with phosphine ligands. In toluene solution the reaction with PBu_3 gives the isomers **2a**–**2c** in the ratio 1.0:2.6:1.2. However, if the reaction is carried out in dichloromethane the isomer ratio is 1.0:9.5:5.8. It is clear that nucleophilic attack by PBu_3 at an osmium atom co-ordinated to

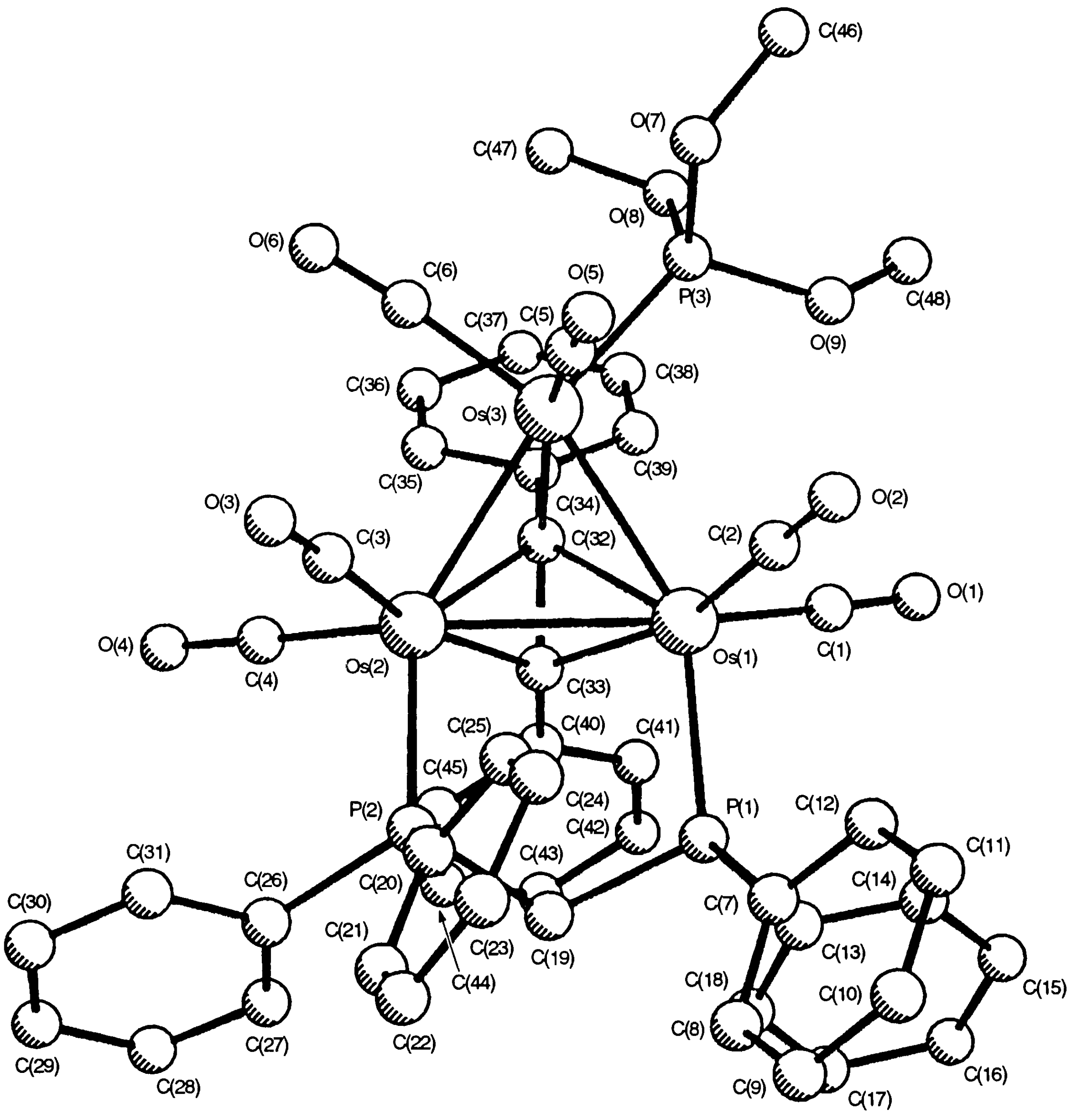


Fig. 3 Molecular structure of $[Os_3(CO)_6(PhC_2Ph)(dppm)\{P(OMe)_3\}]$ **6** with H atoms omitted

one end of the dppm ligand in **1** is strongly disfavoured in more polar solvents. Indeed, isomers **3a** and **5a** are not obtained at all when dichloromethane is used as the solvent in the reaction of **1** with PPh_3 or $P(OMe)_3$, respectively. This reinforces the evidence of the structural studies of complex **1**[2] (and **6**) that the unsaturated nature of the cluster is delocalised over all the osmium atoms.

Experimental

All reactions were carried out under nitrogen using dried, degassed solvents. Infrared spectra were recorded on a Perkin-Elmer 681 spectrophotometer using CH_2Cl_2 solutions, mass spectra on a VG7070E instrument, and NMR spectra in $CDCl_3$ using Bruker WM250 or AMX400 instruments. Chemical shifts are relative to 85% H_3PO_4 for ^{31}P. Microanalyses were carried out in the Department of Chemistry, University of Liverpool. The compound $[Os_3(CO)_7(PhC_2Ph)(dppm)]$ **1** was prepared as previously described.[3]

Reactions of compound 1

With PBu_3. Tributylphosphine (0.10 g, 0.49 mmol) was added to a solution of compound **1** (0.652 g, 0.49 mmol) in toluene (20 cm^3) with stirring, at room temperature. After 2 h the solution had changed from red to orange. It was evaporated to dryness and the residue subjected to TLC [SiO_2; eluent CH_2Cl_2–heptane (4:1 v/v)]. This gave one band which yielded complex $[Os_3(CO)_7(PhC_2Ph)(dppm)(PBu_3)]$ **2** as a mixture of three isomers **a**–**c** (0.57 g, 76%). On recrystallisation from CH_2Cl_2–heptane, orange crystals of **2a** and red crystals of **2c** were separated for crystallographic analysis but in insufficient amounts for spectroscopic analysis (Found: C, 45.9; H, 4.1%; M^+ 1531. $C_{58}H_{59}O_7Os_3P_3$ requires C, 45.5; H, 3.9%; M 1531).

With PPh_3. Triphenylphosphine (0.038 g, 0.145 mmol) was added to a solution of compound **1** (0.194 g, 0.146 mmol) in toluene (20 cm^3) with stirring, at room temperature. After 24 h the solution had changed from red to orange. It was evaporated to dryness and the residue separated by TLC [CH_2Cl_2–heptane (1:1 v/v)] which gave three bands. The major orange band was characterised as $[Os_3(CO)_7(PhC_2Ph)(dppm)(PPh_3)]$ **3** (0.062 g, 31%) (Found: C, 47.6; H, 3.2%; M^+ 1592. $C_{64}H_{47}O_7Os_3P_3$ requires C, 48.2; H, 2.95%; M 1592). A second orange band and a yellow band were isolated in trace amounts and thus were unable to be characterised.

With PMe_2Ph. To a solution of compound **1** (0.205 g, 0.154 mmol) in toluene (20 cm^3) was added 1 equivalent of PMe_2Ph (0.0213 g, 0.154 mmol) and the solution was stirred at room temperature for 1 h. The resulting orange solution was evaporated to dryness and the residue subjected to TLC

Table 5 Fractional atomic coordinates for $[Os_3(CO)_7(PhC_2Ph)(dppm)(PBu_3)]$ **2a**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.336 08(5)	0.233 15(3)	0.833 38(5)	C(24)	0.765(2)	0.124(1)	1.287(2)
Os(2)	0.388 73(5)	0.272 80(3)	1.083 32(5)	C(25)	0.705(2)	0.154(1)	1.187(2)
Os(3)	0.338 27(5)	0.144 18(3)	1.000 15(6)	C(26)	0.648(1)	0.339 9(8)	1.092(1)
P(1)	0.519 3(3)	0.231 3(2)	0.807 4(3)	C(27)	0.756(1)	0.334(1)	1.076(2)
P(2)	0.578 2(3)	0.265 2(2)	1.080 7(3)	C(28)	0.811(2)	0.387(1)	1.078(2)
P(3)	0.242 4(3)	0.275 1(2)	0.654 1(3)	C(29)	0.757(2)	0.451(1)	1.098(2)
O(1)	0.345(1)	0.092 6(6)	0.696(1)	C(30)	0.649(2)	0.460(1)	1.120(2)
O(2)	0.315(1)	0.385 5(6)	0.892(1)	C(31)	0.596(2)	0.402(1)	1.116(2)
O(3)	0.327(1)	0.418 5(7)	1.160(1)	C(32)	0.615(1)	0.217 9(7)	0.947(1)
O(4)	0.431(1)	0.246 2(7)	1.339(1)	C(33)	0.205(1)	0.223 4(8)	0.922(1)
O(5)	0.345(1)	0.107 6(8)	1.250(1)	C(34)	0.234(1)	0.243 1(7)	1.041(1)
O(6)	0.225(1)	0.021 3(8)	0.896(1)	C(35)	0.090(1)	0.210 7(8)	0.864(1)
O(7)	0.554(1)	0.060 2(7)	0.976(1)	C(36)	0.005(1)	0.258 4(9)	0.882(1)
C(1)	0.341(1)	0.144 3(8)	0.754(1)	C(37)	−0.099(1)	0.253(1)	0.831(2)
C(2)	0.329(1)	0.327 5(8)	0.893(1)	C(38)	−0.121(2)	0.198(1)	0.758(2)
C(3)	0.356(1)	0.361 8(9)	1.129(1)	C(39)	−0.042(2)	0.148(1)	0.736(2)
C(4)	0.414(1)	0.254 9(8)	1.238(1)	C(40)	0.065(1)	0.153 8(9)	0.791(1)
C(5)	0.341(1)	0.120(1)	1.153(2)	C(41)	0.152(1)	0.249 8(8)	1.125(1)
C(6)	0.264(2)	0.068(1)	0.934(2)	C(42)	0.128(1)	0.309(1)	1.189(2)
C(7)	0.474(1)	0.094 4(9)	0.987(1)	C(43)	0.048(2)	0.321(1)	1.262(2)
C(8)	0.570(1)	0.303 4(8)	0.763(1)	C(44)	−0.007(2)	0.268(1)	1.265(2)
C(9)	0.626(1)	0.298(1)	0.668(2)	C(45)	0.014(2)	0.209(1)	1.209(2)
C(10)	0.663(2)	0.357(1)	0.641(2)	C(46)	0.096(1)	0.198(1)	1.134(2)
C(11)	0.647(2)	0.419(1)	0.708(2)	C(47)	0.227(1)	0.213 0(9)	0.523(1)
C(12)	0.593(2)	0.422(1)	0.802(2)	C(48)	0.144(1)	0.165 6(9)	0.519(1)
C(13)	0.552(1)	0.365(1)	0.824(1)	C(49)	0.164(2)	0.102(1)	0.435(2)
C(14)	0.566(1)	0.160 9(8)	0.704(1)	C(50)	0.083(2)	0.052(1)	0.447(2)
C(15)	0.635(1)	0.106 1(9)	0.741(1)	C(51)	0.311(1)	0.340 0(9)	0.607(1)
C(16)	0.659(2)	0.054(1)	0.658(2)	C(52)	0.255(2)	0.375(1)	0.501(2)
C(17)	0.616(2)	0.055(1)	0.540(2)	C(53)	0.321(2)	0.432(1)	0.473(2)
C(18)	0.550(2)	0.110(1)	0.505(2)	C(54)	0.331(3)	0.486(2)	0.558(4)
C(19)	0.523(1)	0.162(1)	0.585(2)	C(55)	0.102(1)	0.313 7(9)	0.648(1)
C(20)	0.668(1)	0.220 7(8)	1.200(1)	C(56)	0.084(2)	0.376(1)	0.729(2)
C(21)	0.694(1)	0.257(1)	1.309(2)	C(57)	−0.035(2)	0.411(1)	0.705(2)
C(22)	0.755(2)	0.226(1)	1.407(2)	C(58)	−0.058(3)	0.469(2)	0.802(3)
C(23)	0.788(2)	0.162(1)	1.393(2)				

Table 6 Fractional atomic coordinates for $[Os_3(CO)_6(PhC_2Ph)(dppm)\{P(OMe)_3\}]$ **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	0.525 03(3)	0.400 07(4)	0.338 07(3)	C(18)	0.568(1)	0.724(1)	0.299 5(8)
Os(2)	0.567 13(3)	0.309 98(4)	0.224 78(3)	C(19)	0.650 1(8)	0.535(1)	0.272 5(7)
Os(3)	0.498 06(3)	0.207 30(4)	0.305 06(3)	C(20)	0.766 1(9)	0.377(1)	0.307 2(7)
P(1)	0.615 1(2)	0.530 1(3)	0.348 3(2)	C(21)	0.839 0(8)	0.410(1)	0.304 7(7)
P(2)	0.674 2(2)	0.413 5(3)	0.241 8(2)	C(22)	0.910(1)	0.387(1)	0.357 7(8)
P(3)	0.403 9(2)	0.168 1(3)	0.357 0(2)	C(23)	0.905(1)	0.334(1)	0.414(1)
O(1)	0.408 2(6)	0.507 5(8)	0.395 4(6)	C(24)	0.833(1)	0.300(1)	0.420 3(8)
O(2)	0.594 0(7)	0.297 7(8)	0.479 1(6)	C(25)	0.763 4(9)	0.324(1)	0.365 3(8)
O(3)	0.679 5(6)	0.132 6(8)	0.255 2(6)	C(26)	0.704 1(8)	0.436(1)	0.163 5(7)
O(4)	0.537 4(7)	0.280 2(9)	0.068 6(6)	C(27)	0.681(1)	0.519(1)	0.123 6(8)
O(5)	0.616 8(7)	0.089(1)	0.416 2(6)	C(28)	0.692(1)	0.524(1)	0.058 1(8)
O(6)	0.462 0(7)	0.034 9(8)	0.204 4(6)	C(29)	0.729(1)	0.450(1)	0.033 8(9)
O(7)	0.428 3(6)	0.068 8(8)	0.401 1(6)	C(30)	0.753(1)	0.367(1)	0.073 3(9)
O(8)	0.313 8(6)	0.152 6(8)	0.311 2(6)	C(31)	0.741(1)	0.361(1)	0.138 1(9)
O(9)	0.390 5(6)	0.247 3(8)	0.410 9(5)	C(32)	0.448 0(8)	0.339(1)	0.237 5(7)
C(1)	0.453(1)	0.468(1)	0.372 9(9)	C(33)	0.488 9(7)	0.424(1)	0.228 8(6)
C(2)	0.569(1)	0.336(1)	0.425 7(8)	C(34)	0.361 7(8)	0.325(1)	0.200 7(7)
C(3)	0.635(1)	0.198(1)	0.244 5(8)	C(35)	0.339 1(9)	0.285(1)	0.131 7(8)
C(4)	0.547 8(9)	0.294(1)	0.129(1)	C(36)	0.259(1)	0.273(1)	0.094 3(8)
C(5)	0.571(1)	0.132(1)	0.373(1)	C(37)	0.202(1)	0.296(1)	0.126 5(8)
C(6)	0.475(1)	0.098(1)	0.244 9(9)	C(38)	0.224(1)	0.335(1)	0.190 6(8)
C(7)	0.705 5(8)	0.534(1)	0.423 1(7)	C(39)	0.302 2(9)	0.350(1)	0.227 9(8)
C(8)	0.775(1)	0.579(1)	0.418 1(8)	C(40)	0.454 2(8)	0.513(1)	0.186 1(7)
C(9)	0.842(1)	0.581(1)	0.478(1)	C(41)	0.411(1)	0.579(1)	0.206 4(8)
C(10)	0.840(1)	0.540(1)	0.539 6(8)	C(42)	0.381(1)	0.664(1)	0.169(1)
C(11)	0.772(1)	0.500(1)	0.545 4(8)	C(43)	0.401(1)	0.683(1)	0.109(1)
C(12)	0.704 1(9)	0.496(1)	0.485 9(8)	C(44)	0.444(1)	0.619(1)	0.086(1)
C(13)	0.575 7(8)	0.654(1)	0.351 0(7)	C(45)	0.473 3(9)	0.531(1)	0.125 2(8)
C(14)	0.551 5(9)	0.679(1)	0.406 5(8)	C(46)	0.381(1)	0.029(1)	0.443(1)
C(15)	0.520 7(9)	0.771(1)	0.414 8(8)	C(47)	0.293(1)	0.094(1)	0.248 6(9)
C(16)	0.513(1)	0.841(1)	0.363 2(8)	C(48)	0.317(1)	0.272(1)	0.420(1)
C(17)	0.537(1)	0.819(1)	0.304 8(8)				

[CH_2Cl_2–heptane (2:1 v/v)] which gave three bands. The major orange band was characterised as [$Os_3(CO)_7(PhC_2Ph)$-(dppm)(PMe_2Ph)] **4** (0.057 g, 41%) on the basis of ^{31}P NMR and IR spectroscopy (Found: M^+ 1468. $C_{54}H_{43}O_7Os_3P_3$ requires M 1468). A second orange band and a yellow band contained insufficient material for characterisation.

With $P(OMe)_3$. Trimethyl phosphite (0.0089 g, 0.007 mmol) was added to a toluene solution (20 cm^3) of compound **1** (0.095 g, 0.007 mmol) at room temperature. An instantaneous change from red to orange occurred. The solution was evaporated to dryness and the residue separated by TLC [CH_2Cl_2–heptane (1:1 v/v)]. One band was isolated which yielded complex **5** (0.071 g, 70%) (Found: C, 40.3; H, 3.6%; $M + H^+$ 1453. $C_{49}H_{41}O_{10}Os_3P_3$ requires C, 40.3; H, 2.8%; M 1452). Over several weeks at room temperature a solution of **5** in CH_2Cl_2–heptane darkened to red, and red crystals of **6** were isolated (Found: M^+ 1424. $C_{48}H_{41}O_9Os_3P_3$ requires M 1424); IR spectrum in CH_2Cl_2 2018s, 1965vs, 1934s and 1903m cm^{-1}.

Reaction of compound 6 with CO

Carbon monoxide was bubbled through a stirred solution of complex **6** (0.071 g, 0.05 mmol) in toluene (15 cm^3) at room temperature until it became orange (3 h). The ^{31}P NMR spectrum showed complete conversion of **6** into the clusters **5b** and **5c**. Refluxing this toluene solution under nitrogen for 0.5 h resulted in complete conversion into **6** on the basis of ^{31}P NMR data.

X-Ray crystallography

Crystals of compounds **2a**, **2c** and **6** were mounted on glass fibres. Using a Rigaku AFC6S diffractometer and Mo-Kα radiation $\lambda = 0.710\,73$ Å, cell dimensions were obtained by least-squares refinement of 25 reflections for **2a**, 16 reflections for **2c** and 20 reflections for **6**. Crystal data and experimental details are given in Table 4. The TEXSAN structure analysis package was used.[8]

Structure analysis and refinement. For compound **2a** the structure was solved by direct methods. The Os, P and O atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and given isotropic thermal parameters 20% greater than the B(equivalent) value of the atom to which they were bonded. Full-matrix least-squares refinement. Final fractional atomic coordinates are given in Table 5.

For compound **2c** the structure was solved by direct methods. The quality of the data was poor due to 73% decomposition as monitored by the intensities of three representative reflections measured after every 150. A linear correction factor was applied, however the full structure could not be refined. The atoms not located were eight of the 12 C atoms of the PBu_3 group. Also, the carbonyl C atoms, although located, did not refine satisfactorily. In view of this the structure determination was only used to define the sites of co-ordination of the dppm, PBu_3 and PhC_2Ph ligands.

For compound **6** the structure was solved and refined as for **2a**. Final fractional atomic coordinates are given in Table 6.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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