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The use of bis(diphenylphosphinoacetylene) and its digold derivative as linking groups in osmium cluster chemistry. Crystal structures of $[\{Os_3(CO)_{11}\}_2(dppa)]$, $[Os_3(CO)_{10}(dppa)]_2$ and $[Os_4H(CO)_{12}Au(dppa)]_2$ (dppa = $Ph_2PC{\equiv}CPPh_2$)

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Abstract

The reaction of the activated triosmium cluster, $[Os_3(CO)_{11}(NCMe)]$ with bis(diphenylphosphinoacetylene) (dppa) at room temperature affords the linked cluster $[\{Os_3(CO)_{11}\}_2(dppa)]$ (1), while the reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with an excess of dppa affords the di-, tri- and tetrameric clusters $[\{Os_3(CO)_{10}(dppa)\}_2]$ (2), $[\{Os_3(CO)_{10}(dppa)\}_3]$ (3) and $[\{Os_3(CO)_{10}(dppa)\}_4]$ (4) in moderate yields. Similarly, the reaction of the anion $[Os_4H_3(CO)_{12}]^-$ with $Au_2(dppa)Cl_2$, in the presence of excess Et_3N and $TlPF_6$, under reflux, in chloroform affords $[\{Os_4H(CO)_{12}Audppa\}_2]$ (5) as the only extractable product. Single crystal X-ray structural analyses of 1 and 2 show that the two triosmium cluster units are linked *via* coordination of one Os centre to each of the two phosphorus centres of the intact dppa ligand, while the structure of 5 shows the two tetraosmium units are linked *via* two μ_2-bridging Au centres and terminal phosphorus centres of the two Au(dppa) ligands.

Introduction

Bis(diphenylphosphinoacetylene) (dppa) has been reported as a potential trifunctional ligand which normally coordinates *via* its two phosphorus centres, leaving the acetylenic bond coordinatively inactive [1]. The rigidity of the linear $-C{\equiv}C-$ unit and the long P–P distance of 4.7 Å in the P–C–C–P skeleton of dppa prevents chelation to one metal centre or across a metal–metal bond. The typical behaviour of this di-substituted acetylene is to form bridged binuclear or polymeric complexes in which only the phosphorus atoms of the ligand are coordinated [2–4]. Previous reports of the interaction between triruthenium clusters and dppa indicate that P–C bond cleavage as well as metal–metal bond cleavage occurs readily

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upon heating [5,6], and a mixture of tetra- and penta-ruthenium clusters is obtained. However, under mild reaction conditions, in the presence of an activated cluster complex, the dppa ligand has the potential to act as a linking group between cluster units and facilitate cluster build-up.

In view of previous work with ruthenium clusters, it was decided to undertake a series of reactions between osmium carbonyl and dppa in the expectation of forming oligomeric species that are relatively inert kinetically which might be of interest as intermediates in the synthesis of high-nuclearity cluster complexes. We now report the synthesis of oligomeric species containing triosmium cluster units linked by intact dppa ligands, and in an extension of the work, the use of a digold-bidentate phosphine fragment to link anionic cluster fragments, which are not susceptible to linkage when a neutral bidentate phosphine is used.

Results and discussion

The activated triosmium cluster $[Os_3(CO)_{11}(NCMe)]$ reacted with dppa (2:1 molar ratio) during 2 h in dichloromethane at room temperature to afford a dark yellow product (*ca.* 60% yield) which was shown to be the dimeric species $[\{Os_3(CO)_{11}\}_2(dppa)]$ (**1**). The $^{31}P\{^1H\}$ NMR spectrum of **1** exhibits a singlet at δ −171.67 [reference $P(OMe)_3$]. This signal shows a high field shift relative to the signal of the free dppa ligand (107 ppm) [7] on coordinating to the metal centres. The appearance of a singlet resonance is taken to indicate that the two phosphorus atoms in the dppa ligand are in equivalent environments and that each phosphorus is coordinated to a single metal centre. The ^1H NMR spectrum in CD_2Cl_2 shows a multiplet at δ 7.48 due to the phenyl resonance and the FAB mass spectrum exhibits an envelope with a molecular ion peak at 2155. The spectroscopic data for **1**, presented in Table 1 is consistent with the solid state structure.

To confirm the spectroscopic assignments a single crystal X-ray structure determination was carried out on an orange crystal of **1** obtained by slow diffusion of acetonitrile into a solution of dichloromethane/hexane at room temperature during 2 days. The molecular structure of **1** is shown in Fig. 1, together with the atomic labelling scheme. Some selected bond distances and bond angles are listed in Table 2. The structure of **1** consists of two triosmium triangles symmetrically

Table 1

Spectroscopic data for compounds **1**–**5**

Compound	IR (ν CO, cm^{-1}, hexane)	MS *m/e*	$^{31}P\{^1H\}$ NMR [a] CD_2Cl_2	^1H NMR CD_2Cl_2
$[\{Os_3(CO)_{11}\}_2(dppa)]$	2109m, 2057s, 2021vs,	2155	−171.67(s)	7.46 m
$[\{Os_3(CO)_{10}(dppa)\}_2]$	2095w, 2069vs	2488	−166.31(s), −173.30(s)	7.45m
$[\{Os_3(CO)_{10}(dppa)\}_3]$	2088w, 2070w, 2059w, 2033m, 2004vs, 1974m,	3735	−174.16(s)	7.50 m
$[\{Os_3(CO)_{10}(dppa)\}_4]$	2033m, 2004vs, 1974m,	4979		7.50 m
$[\{HOs_4(CO)_{12}Audppa\}_2]$	2069s, 2033vs, 2020vs, 1988m, 1965w, 1932m	3378	−149.0(s), −84.6(s)	−20.51(s)

[a] ^{31}P NMR reference P(OMe).

Table 2

Selected bond distances (Å) and angles (°) for $[\{Os_3(CO)_{11}\}_2(dppa)]$ (**1**)

Os(1)-Os(2)	2.876(3)	Os(1)-Os(3)	2.907(3)
Os(2)-Os(3)	2.883(3)	Os(4)-Os(5)	2.877(3)
Os(4)-Os(6)	2.903(3)	Os(5)-Os(6)	2.881(3)
Os(1)-P(1)	2.336(11)	Os(4)-P(2)	2.321(12)
P(1)-C(1)	1.78(5)	P(1)-C(1a)	1.87(4)
P(1)-C(2a)	1.82(4)	P(2)-C(2)	1.81(5)
P(2)-C(3a)	1.92(4)	P(2)-C(4a)	1.83(4)
C(1)-C(2)	1.13(7)		
Os(2)-Os(1)-Os(3)	59.8(1)	Os(1)-Os(2)-Os(3)	60.6(1)
Os(1)-Os(3)-Os(2)	59.6(1)	Os(5)-Os(4)-Os(6)	59.8(1)
Os(4)-Os(5)-Os(6)	60.6(1)	Os(4)-Os(6)-Os(5)	59.7(1)
Os(2)-Os(1)-P(1)	168.4(3)	Os(3)-Os(1)-P(1)	108.8(3)
Os(5)-Os(4)-P(2)	168.0(3)	Os(6)-Os(4)-P(2)	108.6(3)
Os(1)-P(1)-C(1)	115(1)	Os(4)-P(2)-C(2)	115(1)
P(1)-C(1)-C(2)	173(4)	P(2)-C(2)-C(1)	173(4)
Os(2)-Os(1)-C(11)	88(1)	Os(2)-Os(1)-C(12)	93(1)
Os(3)-Os(1)-C(11)	95(1)	Os(1)-Os(2)-C(21)	93(1)
Os(1)-Os(2)-C(22)	87(1)	Os(3)-Os(2)-C(21)	90(1)
Os(3)-Os(2)-C(22)	84(1)	Os(1)-Os(3)-C(31)	87(2)
Os(1)-Os(3)-C(32)	94(2)	Os(2)-Os(3)-C(31)	86(2)
Os(2)-Os(3)-C(32)	90(2)	Os(5)-Os(4)-C(42)	93(1)
Os(5)-Os(4)-C(43)	87(2)	Os(6)-Os(4)-C(42)	82(1)
Os(6)-Os(4)-C(43)	95(2)	Os(4)-Os(5)-C(51)	84(1)
Os(4)-Os(5)-C(54)	91(1)	Os(6)-Os(5)-C(51)	94(1)
Os(6)-Os(5)-C(54)	86(2)	Os(4)-Os(6)-C(61)	92(1)
Os(4)-Os(6)-C(63)	88(1)	Os(5)-Os(6)-C(61)	84(1)
Os(5)-Os(6)-C(63)	92(1)		

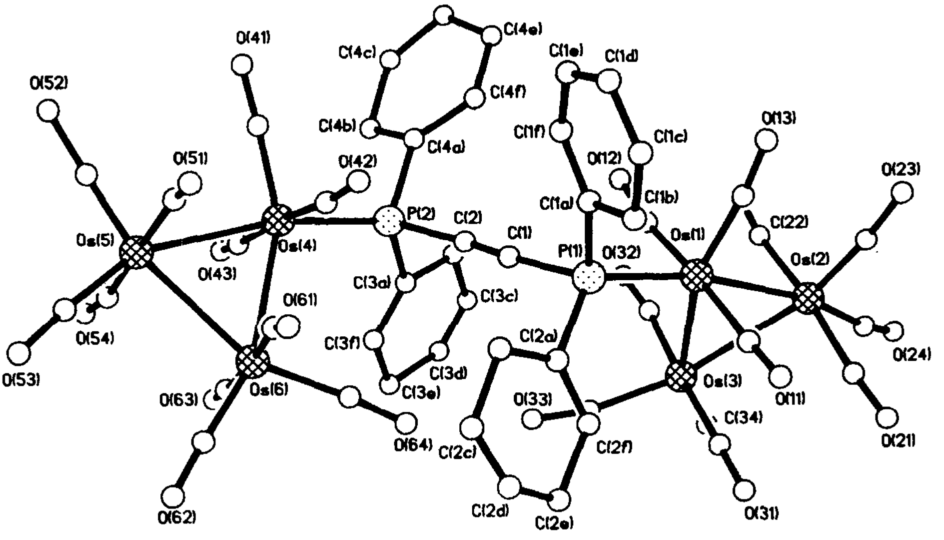

Fig. 1. The molecular structure of $[\{Os_3(CO)_{11}\}_2(dppa)]$ (1)

linked by the phosphinoacetylene ligand which coordinates *via* the two phosphorus centres and occupies equatorial sites on one osmium atom in each triosmium cluster. The Os(1)–Os(3) and Os(4)–Os(6) distances (average 2.905(3) Å) are significantly longer than all other Os–Os distances (average 2.879(3) Å). This may be due to the steric repulsion between the bulky dppa ligand and the adjacent equatorial carbonyl ligands. This pronounced steric crowding in the neighbourhood of the central C≡C triple bond apparently leads to the observed bending of the central P–C≡C–P linkage; the phosphorus atoms are no longer colinear with the acetylenic C≡C bond (Table 2).

Treatment of the triosmium cluster, $[Os_3(CO)_{10}(NCMe)_2]$ with a three-fold excess of dppa, in dichloromethane, proceeds at room temperature over a period of 12 h to produce oligomeric species, $[\{Os_3(CO)_{10}(dppa)\}_2]$ (**2**), $[\{Os_3(CO)_{10}(dppa)\}_3]$ (**3**) and $[\{Os_3(CO)_{10}(dppa)\}_4]$ (**4**) which have been characterised on the basis of FAB mass spectra which show molecular ion peaks at 2486 (calculated $m/e = 2488$), 3735 (calculated $m/e = 3734$) and at 4979 (calculated $m/e = 4978$) for **2–4** respectively. The $^{31}P\{^1H\}$ NMR of **2** shows signals at δ −166.31 and −173.30 suggesting the presence of two inequivalent phosphorus atoms in the molecule. The ^1H NMR spectrum shows a multiplet at δ 7.45 due to the phenyl resonance. For structural characterisation of this dimeric species **2** an X-ray diffraction study was carried out on a single crystal obtained by the solvent diffusion method (acetonitrile into dichloromethane/hexane). The molecular structure of $[\{Os_3(CO)_{10}(dppa)\}_2]$ (**2**) shows a sterically strained molecule, where the two triosmium clusters are linked through two dppa ligands in a ring fashion. This structural analysis provided further support for the earlier suggestion that the dppa ligand does not undergo chelation. It is interesting to note that even under such unfavourably strained conditions the dppa ligand links two triosmium clusters. The molecular structure of **2** with its atomic labelling scheme is shown in Fig. 2, and some important bond lengths and bond angles are presented in Table 3. It is noteworthy that the carbonyls in **1** and **2** are significantly different in orientation. The axial carbonyls in **1** are essentially perpendicular to the Os_3 triangle, however, those in **2** are no longer perpendicular to the triosmium unit, probably because of the severe steric crowding of the molecule.

The $^{31}P\{^1H\}$ NMR spectra of **3** shows a singlet at δ −174.16 suggesting that the phosphorus atoms are in identical environments, and hence a symmetrical arrangement of the phosphinoacetylene in the trimer is expected. However, no satifactory ^{31}P NMR spectrum has been obtained for **4**. The most probable structures of the oligomers **3** and **4** are shown in Fig. 3.

In an attempt to synthesise the compound $[Os_4H_2(CO)_{12}(AuPR_3)_2]$ [8] with dppa instead of with monodentate phosphine, $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$ was treated with $Au_2dppaCl_2$ in the presence of excess Et_3N (to aid in the formation of the dianion, $[Os_4H_2(CO)_{12}]^{2-}$) and $TlPF_6$ (as a halide acceptor) in $CHCl_3$ under reflux, to give a red compound as the only product isolated (*ca.* 30%) after chromatography on silica (a thin layer of purple material deposited on the inner surface of the reaction flask was not characterised). Fast atom bombardment mass spectrum of this red compound gives a molecular ion at m/z 3378 which does not fit the expected product $[\{Os_4H_2(CO)_{12}(Au_2dppa)\}_2]$ (calculated 3374). To establish the identity, a single crystal X-ray diffraction study of this compound was undertaken. It revealed a molecular formula of $[\{Os_4H(CO)_{12}(Audppa)\}_2]$ (**5**) for

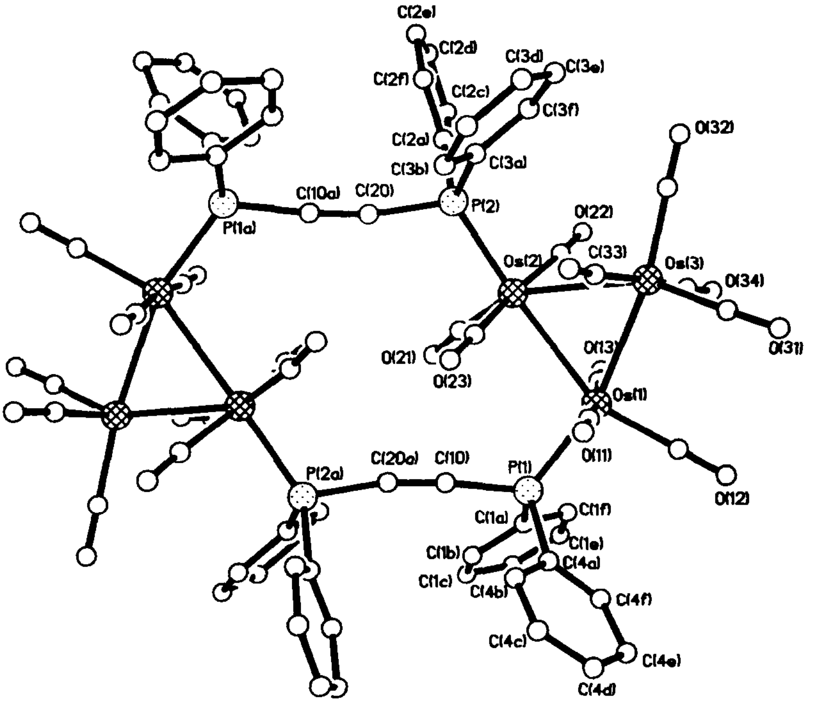

Fig. 2. The molecular structure of $[\{Os_3(CO)_{10}(dppa)\}_2]$ (**2**)

this red compound, which is consistent with all the spectroscopic and analytical data. The molecular structure of **5** is shown in Fig. 4. Some selected bond parameters are listed in Table 4. The structure consists of two tetrahedral Os_4

Table 3

Selected bond distances (Å) and angles (°) for $[\{Os_3(CO)_{10}(dppa)\}_2]$ (**2**)

Os(1)–Os(2)	2.896(2)	Os(1)–Os(3)	2.865(2)
Os(2)–Os(3)	2.909(2)	Os(1)–P(1)	2.330(4)
Os(2)–P(2)	2.328(4)	P(1)–C(10)	1.76(1)
P(1)–C(1a)	1.84(2)	P(1)–C(4a)	1.83(2)
P(2)–C(20)	1.79(1)	P(2)–C(2a)	1.85(2)
P(2)–C(3a)	1.83(2)	C(10)–C(20a)	1.22(2)
Os(2)–Os(1)–Os(3)	60.6(1)	Os(1)–Os(2)–Os(3)	59.1(1)
Os(1)–Os(3)–Os(2)	60.2(1)	Os(2)–Os(1)–P(1)	105.4(1)
Os(3)–Os(1)–P(1)	162.4(1)	Os(1)–Os(2)–P(2)	161.1(1)
Os(3)–Os(2)–P(2)	110.0(1)	Os(1)–P(1)–C(10)	118.5(5)
Os(2)–P(2)–C(20)	115.6(4)	P(1)–C(10)–C(20a)	175.2(12)
P(2)–C(20)–C(10a)	169.6(12)	Os(2)–Os(1)–C(11)	95.7(4)
Os(2)–Os(1)–C(13)	77.8(4)	Os(3)–Os(1)–C(11)	83.1(4)
Os(3)–Os(1)–C(13)	92.4(4)	Os(1)–Os(2)–C(22)	95.7(4)
Os(1)–Os(2)–C(23)	79.6(4)	Os(3)–Os(2)–C(22)	73.1(5)
Os(3)–Os(2)–C(23)	97.8(5)	Os(1)–Os(3)–C(33)	93.0(5)
Os(1)–Os(3)–C(34)	82.5(5)	Os(2)–Os(3)–C(33)	74.5(5)
Os(2)–Os(3)–C(34)	98.8(6)		

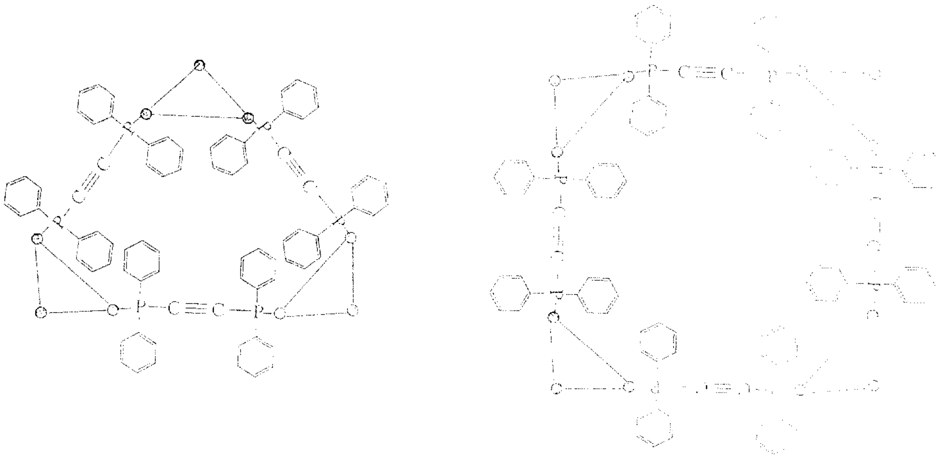

Fig. 3. Probable structures of [{Os$_3$(CO)$_{10}$(dppa)}$_3$] (3) and [{Os$_3$(CO)$_{10}$(dppa)}$_4$] (4)

units linked by two Audppa moieties. The gold atom of the Audppa group bridges one edge of the Os$_4$ cluster unit while the phosphorus atom at the other end of the Audppa unit coordinates to one of the Os atoms of another Os$_4$ cluster to form a linkage between two Os$_4$ units. The same linkage is present at the other end of the two Os$_4$ clusters so that the compound **5** has a cyclic arrangement as observed in

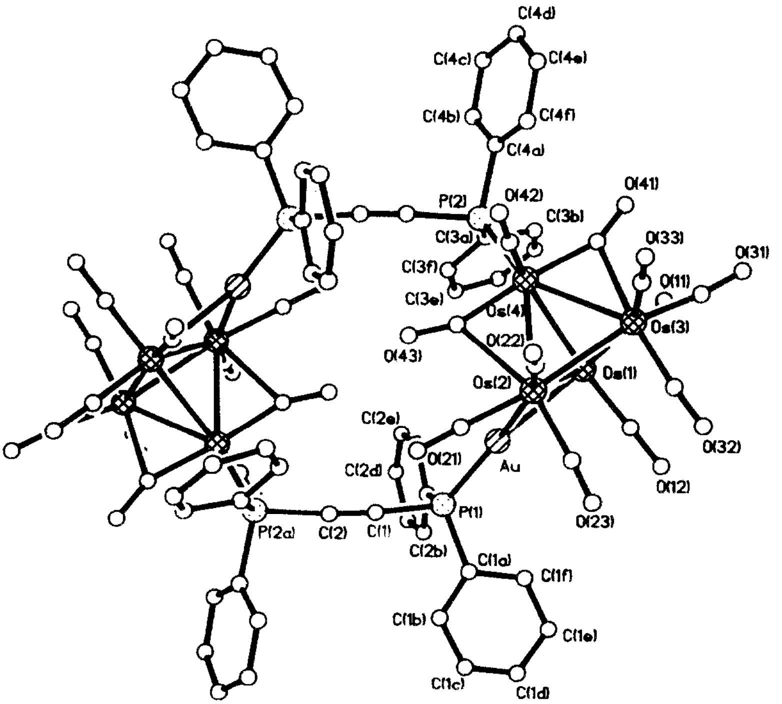

Fig. 4. The molecular structure of [{Os$_4$H(CO)$_{12}$(Audppa)}$_2$] (5)

Table 4

Selected bond distances (Å) and angles (°) for $[\{Os_4H(CO)_{12}(Audppa)\}_2]$ (**5**)

Os(1)-Os(2)	2.933(3)	Os(1)-Os(3)	2.819(3)
Os(1)-Os(4)	2.976(3)	Os(2)-Os(3)	2.832(3)
Os(2)-Os(4)	2.834(3)	Os(3)-Os(4)	2.812(2)
Os(1)-Au	2.744(3)	Os(2)-Au	2.784(3)
Au-P(1)	2.277(10)	Os(3)-C(41)	2.37(3)
Os(4)-C(41)	1.95(3)	Os(3)-C(43)	2.59(3)
Os(4)-C(43)	1.93(4)	P(1)-C(1)	1.79(4)
P(2a)-C(2)	1.81(3)	C(1)-C(2)	1.15(4)
Os(2)-Os(1)-Os(3)	58.9(1)	Os(2)-Os(1)-Os(4)	57.3(1)
Os(3)-Os(1)-Os(4)	58.0(1)	Os(1)-Os(2)-Os(3)	58.5(1)
Os(1)-Os(2)-Os(3)	58.5(1)	Os(1)-Os(2)-Os(4)	62.1(1)
Os(3)-Os(2)-Os(4)	59.5(1)	Os(1)-Os(3)-Os(2)	62.5(1)
Os(1)-Os(3)-Os(4)	63.8(1)	Os(2)-Os(3)-Os(4)	60.3(1)
Os(1)-Os(4)-Os(2)	60.6(1)	Os(1)-Os(4)-Os(3)	58.2(1)
Os(2)-Os(4)-Os(3)	60.2(1)	Os(1)-Au-Os(2)	64.1(1)
Os(1)-Au-P(1)	149.8(2)	Os(2)-Au-P(1)	145.7(3)
Os(3)-C(41)-Os(4)	80(1)	Os(3)-C(41)-O(41)	126(2)
Os(4)-C(41)-O(41)	153(2)	Os(2)-C(43)-Os(4)	76(1)
Os(2)-C(43)-O(43)	124(3)	Os(4)-C(43)-O(43)	159(3)
P(1)-C(1)-C(2)	172(4)	P(2a)-C(2)-C(1)	173(4)

compound **2**. There are two asymmetric bridging CO ligands in each Os_4 units. It is worth noting that the reaction involves the loss of two H atoms and the addition of a phosphine, so that **5** may be considered as a substituted derivative of the $[Os_4H(CO)_{13}]^-$ anion. The $^{31}P\{^1H\}$ NMR spectrum of **5** shows two singlets at -149.0 ppm and -84.6 ppm which have been assigned to the phosphorus coordinated to the osmium atom and the gold atom respectively. The ^1H NMR of **5** in CD_2Cl_2 shows only one singlet at -20.51 ppm at room temperature and -50°C. However, the hydride atom cannot be located reliably from X-ray analysis or potential energy calculations [9]. The formation of **5** inevitably involves the loss of one Au atom from $Au_2dppaCl_2$. It has not been possible to establish the fate of this gold atom although it might be contained in the purple material deposited.

Experimental

Materials and methods

All reactions were carried out under dry nitrogen by standard Schlenk and vacuum line techniques. Dichloromethane was dried over CaH_2 and $[Os_3(CO)_{11}(NCMe)]$ [10], $[Os_3(CO)_{10}(NCMe)_2]$ [10], $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$ [11], and $[Au_2dppaCl_2]$ [12] were prepared by published methods. Bis(diphenylphosphinoacetylene), dppa, was used as obtained.

IR spectra were recorded on a Perkin-Elmer 983 or FT 1710 spectrometer using 0.5 mm solution cells. The ^1H NMR and the ^{31}P NMR spectra were recorded on a Bruker WM 250 and a Bruker 400 FT NMR spectrometer respectively. Mass spectra were recorded on an AEI MS 12 or a FAB MS 902 instrument. Routine separations of products were performed by thin layer chromatography on commercially prepared glass plates, precoated to 0.25 mm thickness with Kieselgel 60 F_{254} (Merck).

Synthesis of $[\{Os_3(CO)_{11}\}_2(dppa)]$ *(1)*

A solution of the activated cluster $[Os_3(CO)_{11}(NCMe)]$ (100 mg) in dichloromethane (20 cm^3) was treated with dppa (1.1 eq. 47 mg). The mixture was stirred under nitrogen at room temperature for 2 h. The solvent was removed under vacuum. Purification of the residue by thin layer chromatography with dichloromethane/hexane (20/80) as eluant gave a yellow major product in 60% yield, and this was characterised as $[\{Os_3(CO)_{11}\}_2(dppa)]$ (**1**).

Synthesis of $[\{Os_3(CO)_{10}(dppa)\}_2]$ *(2)*

An excess of dppa as a solid was added to a solution of $[Os_3(CO)_{10}(NCMe)_2]$ (150 mg) in dichloromethane (20 cm^3) and the mixture was stirred for 6 h at room temperature. The solvent was removed *in vacuo*. Purification of the residue by TLC with dichloromethane/hexane (30/70) as eluant afforded three major products in variable yields. The first (orange) band was characterised as $[\{Os_3(CO)_{10}(dppa)\}_2]$ (**2**). The second (orange) band was identified as $[\{Os_3(CO)_{10}(dppa)\}_3]$ (**3**), and the third (yellow) band was characterised as $[\{Os_3(CO)_{10}(dppa)\}_4]$ (**4**).

Table 5

Crystal data and data collection parameters for **1**, **2** and **5**

Compound	**1**	**2**	**5**
Formula	$C_{48}H_{20}O_{22}P_2Os_6$	$C_{72}H_{40}O_{20}P_4Os_6$	$C_{76}H_{40}O_{24}P_4Os_8Au_2$
Colour; habit	Yellow plates	Red plates	Red blocks
Crystal size (mm)	0.10 × 0.44 × 0.52	0.02 × 0.14 × 0.22	0.06 × 0.10 × 0.11
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$ (non-standard No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	12.306(7)	12.033(3)	12.151(8)
b (Å)	31.490(7)	12.294(3)	13.530(8)
c (Å)	14.080(3)	13.301(6)	15.546(10)
α (°)	90.0	77.05(1)	105.90(5)
β (°)	90.27(1)	73.72(1)	102.81(5)
γ (°)	90.0	73.63(1)	113.12(4)
V (Å^3)	5456	1790	2098
Z	4	1	1
Formula wt.	2151.8	2490.1	3376.5
Calc. density (g cm^{-3})	2.619	2.311	2.672
Absorption coeff. (cm^{-1})	140.73	107.84	156.98
$F(000)$	3880	1148	1514
2θ range (°)	5.0–45.0	5.0–45.0	5.0–40.0
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan speed (deg./min.)	2.93–29.3	2.08–29.3	2.93–29.3
Scan range (°)	1.40	1.20	1.20
Reflections collected	7769	5053	4334
Unique reflections	6755	4625	3903
Observed reflections $[F > 4\sigma(F)]$	4156	3667	2983
Absorption correction	Psi-scans	Psi-scans	Psi-scans
Weighting scheme $w = [\sigma^2(F) + gF^2]^{-1}$	g = 0.0020	g = 0.0010	g = 0.0012
R	0.085	0.039	0.048
R_w	0.086	0.040	0.052

Table 6
Final atomic co-ordinates ($\times 10^4$) for $[\{Os_3(CO)_{11}\}_2(dppa)]$ (**1**)

	x	*y*	*z*
Os(1)	6274(2)	1559(1)	4240(1)
Os(2)	6731(2)	1480(1)	2247(1)
Os(3)	5428(2)	842(1)	3168(1)
Os(4)	1480(2)	1387(1)	7858(1)
Os(5)	1035(2)	1118(1)	9770(1)
Os(6)	2467(2)	618(1)	8603(1)
P(1)	5770(10)	1484(4)	5829(8)
P(2)	1969(11)	1460(4)	6277(9)
C(11)	7687(44)	1305(14)	4488(31)
O(11)	8513(43)	1194(14)	4676(30)
C(12)	4909(47)	1767(15)	4017(33)
O(12)	4077(38)	1968(13)	3904(26)
C(13)	6918(42)	2101(14)	4374(30)
O(13)	7214(40)	2454(14)	4480(29)
C(21)	8015(49)	1146(17)	2459(34)
O(21)	8762(55)	957(18)	2460(39)
C(22)	5369(45)	1756(15)	2026(31)
O(22)	4605(36)	1964(12)	1824(25)
C(23)	7530(42)	1929(14)	2225(30)
O(23)	8021(40)	2269(14)	2307(30)
C(24)	6846(43)	1315(14)	917(32)
O(24)	6834(32)	1284(11)	145(24)
C(31)	6710(60)	555(20)	3490(42)
O(31)	7520(41)	375(14)	3697(29)
C(32)	4163(67)	1132(22)	2780(46)
O(32)	3305(42)	1279(14)	2595(30)
C(33)	4716(44)	546(14)	4188(32)
O(33)	4189(32)	431(11)	4788(24)
C(34)	5238(46)	492(15)	2151(33)
O(34)	5091(44)	289(15)	1476(33)
C(41)	770(45)	1907(16)	7983(33)
O(41)	352(40)	2236(14)	8138(29)
C(42)	2898(44)	1622(14)	8210(31)
O(42)	3662(40)	1810(13)	8358(27)
C(43)	158(61)	1117(20)	7493(43)
O(43)	−655(45)	1000(15)	7179(32)
C(51)	2162(41)	1529(14)	10103(29)
O(51)	2863(34)	1674(11)	10405(23)
C(52)	36(51)	1487(17)	10110(36)
O(52)	−666(47)	1797(15)	10425(33)
C(53)	1248(50)	789(17)	10859(37)
O(53)	1405(43)	554(15)	11519(31)
C(54)	−135(47)	732(16)	9323(32)
O(54)	−894(54)	554(18)	9156(38)
C(61)	3639(40)	944(13)	9268(27)
O(61)	4394(34)	1031(11)	9631(24)
C(62)	2669(53)	165(19)	9324(39)
O(62)	2941(45)	−113(16)	9847(32)
C(63)	1294(41)	312(14)	8085(29)
O(63)	558(38)	163(13)	7715(27)
C(64)	3390(55)	507(18)	7573(41)
O(64)	3926(39)	397(13)	6934(28)

Table 6 (continued)

	x	y	z
C(1)	4341(43)	1463(14)	6028(29)
C(2)	3422(44)	1472(14)	6065(30)
C(1A)	6182(40)	1958(13)	6541(28)
C(1B)	7301(53)	1956(18)	6788(38)
C(1C)	7663(56)	2334(19)	7307(39)
C(1D)	6984(49)	2664(16)	7428(34)
C(1E)	5930(59)	2643(19)	7153(41)
C(1F)	5544(49)	2306(17)	6689(34)
C(2A)	6227(39)	1041(13)	6561(28)
C(2B)	6106(50)	1093(17)	7521(36)
C(2C)	6450(43)	688(14)	8064(30)
C(2D)	6909(47)	404(16)	7636(34)
C(2E)	6896(45)	309(15)	6678(31)
C(2F)	6602(42)	703(14)	6116(30)
C(3A)	1553(37)	1029(12)	5381(26)
C(3B)	1408(48)	1216(16)	4428(34)
C(3C)	1134(64)	883(23)	3709(47)
C(3D)	1024(46)	521(15)	3977(32)
C(3E)	1153(53)	312(18)	4963(38)
C(3F)	1412(47)	637(16)	5658(33)
C(4A)	1514(41)	1957(13)	5733(28)
C(4B)	350(65)	1933(21)	5628(45)
C(4C)	9(56)	2367(18)	5224(38)
C(4D)	579(51)	2719(17)	4828(36)
C(4E)	1751(57)	2660(19)	4838(40)
C(4F)	2230(50)	2284(17)	5348(35)

Synthesis of $[\{Os_4H(CO)_{12}Audppa\}_2]$ *(5)*

$Au_2dppaCl_2$ (23 mg) was dissolved in warm $CHCl_3$ (30 cm^3) at 50°C and $N(PPh_3)[H_3Os_4(CO)_{12}]$ (40 mg) in the presence of Et_3N (a few drops) and $TlPF_6$ (excess) was added. The solution was refluxed overnight. Purification of the reaction mixture by TLC with dichloromethane/hexane (60/40) as eluant yielded $[\{Os_4H(CO)_{12}Audppa\}_2]$ as the only extractable product. Red crystals of **5** were obtained in 30% yield with respect to the Au reagent used by slow evaporation of a dichloromethane/hexane solution at room temperature.

Crystal structure determination of $[\{Os_3(CO)_{11}\}_2(dppa)]$ *(1),* $[\{Os_3(CO)_{10}(dppa)\}_2]$ *(2) and* $[\{Os_4H(CO)_{12}(Audppa)\}_2]$ *(5)*

Crystal data and data collection parameters for **1**, **2** and **5** are summarized in Table 5. The intensity data were collected at room temperature on a Siemens R3mV four-circle diffractometer using Mo-K_α radiation ($\lambda = 0.71069$ Å). The structures were solved by a combination of direct methods and Fourier difference techniques and refined by full matrix least-square analysis, with Os and P atoms assigned anisotropic displacement parameters. The hydrogen atoms of the phenyl rings were fixed in calculated positions (C–H 0.96 Å). Detailed experimental procedures for the crystallographic work were as previously described [13]. For all calculations the SHELXTL-PLUS programs were used [14]. Final atomic coordinates for the structures of **1**, **2** and **5** are listed in Tables 6–8.

Table 7

Final atomic co-ordinates ($\times 10^4$) for [$\{Os_3(CO)_{10}(dppa)\}_2$] (**2**)

	x	*y*	*z*
Os(1)	5021(1)	3259(1)	7403(1)
Os(2)	3382(1)	2286(1)	9187(1)
Os(3)	3169(1)	4753(1)	8683(1)
P(1)	6547(3)	1704(3)	6868(3)
P(2)	2320(3)	1809(3)	10912(3)
C(10)	6809(12)	450(12)	7803(12)
C(20)	2944(13)	450(12)	11612(11)
C(1A)	6575(13)	1078(13)	5723(12)
C(1B)	7202(17)	−41(17)	5639(15)
C(1C)	7141(19)	−574(19)	4823(17)
C(1D)	6544(18)	68(18)	4103(17)
C(1E)	5937(18)	1124(18)	4162(16)
C(1F)	5920(15)	1655(15)	4989(13)
C(2A)	794(14)	1607(13)	11192(12)
C(2B)	413(15)	1369(14)	10409(14)
C(2C)	−737(16)	1224(16)	10579(15)
C(2D)	−1469(19)	1273(17)	11583(16)
C(2E)	−1107(20)	1470(18)	12402(18)
C(2F)	68(16)	1634(15)	12208(15)
C(3A)	2185(12)	2733(12)	11865(11)
C(3B)	3002(14)	2504(14)	12488(12)
C(3C)	2915(16)	3280(15)	13180(14)
C(3D)	2033(15)	4258(15)	13200(13)
C(3E)	1239(16)	4524(16)	12522(14)
C(3F)	1306(14)	3743(13)	11901(12)
C(4A)	8009(13)	2031(13)	6540(12)
C(4B)	8733(16)	1725(15)	7218(15)
C(4C)	9774(19)	2117(18)	6996(18)
C(4D)	10079(20)	2762(18)	6040(17)
C(4E)	9411(19)	3071(18)	5287(18)
C(4F)	8365(17)	2673(16)	5592(15)
C(11)	5998(14)	3495(12)	8239(11)
O(11)	6632(10)	3595(11)	8691(10)
C(12)	5535(15)	4434(14)	6285(13)
O(12)	5815(13)	5134(12)	5647(11)
C(13)	3888(15)	2981(13)	6706(12)
O(13)	3279(11)	2838(12)	6283(10)
C(21)	3692(14)	912(14)	8677(12)
O(21)	3868(13)	138(11)	8247(9)
C(22)	1993(16)	2944(13)	8603(11)
O(22)	1159(10)	3213(11)	8254(10)
C(23)	4817(16)	1869(13)	9761(12)
O(23)	5632(11)	1617(11)	10089(10)
C(31)	3806(17)	6064(17)	8195(16)
O(31)	4173(12)	6884(13)	7884(14)
C(32)	1649(16)	5442(15)	9513(15)
O(32)	778(13)	5870(12)	9992(12)
C(33)	3903(16)	4240(13)	9885(16)
O(33)	4328(11)	4078(10)	10592(10)
C(34)	2468(17)	5071(15)	7481(18)
O(34)	2021(14)	5320(12)	6781(11)

Table 8

Final atomic co-ordinates ($\times 10^4$) for $[\{Os_4H(CO)_{12}(Audppa)\}_2]$ **(5)**

	x	y	z
Au	2927(1)	2698(1)	6760(1)
Os(1)	3549(1)	2467(1)	8475(1)
Os(2)	4160(1)	1359(1)	6880(1)
Os(3)	5047(1)	1344(1)	8719(1)
Os(4)	2437(1)	−123(1)	7506(1)
P(1)	2180(7)	3536(7)	5859(6)
P(2)	338(7)	−1187(6)	7441(5)
C(1)	1428(29)	2697(25)	4585(23)
C(2)	806(33)	2128(30)	3781(27)
C(11)	3633(33)	2555(30)	9680(27)
O(11)	3646(24)	2654(22)	10479(20)
C(12)	5033(33)	3870(30)	8922(24)
O(12)	5992(25)	4799(22)	9210(19)
C(13)	2367(36)	3029(32)	8343(27)
O(13)	1749(27)	3508(24)	8456(21)
C(21)	3421(31)	1163(27)	5594(25)
O(21)	3087(24)	999(21)	4774(19)
C(22)	4795(33)	370(30)	6522(26)
O(22)	5204(24)	−235(22)	6210(19)
C(23)	5613(37)	2739(33)	7080(27)
O(23)	6470(29)	3481(26)	7136(21)
C(31)	5642(32)	1789(29)	10038(26)
O(31)	5936(23)	1983(21)	10890(19)
C(32)	6604(36)	2556(32)	8877(26)
O(32)	7581(26)	3327(23)	9045(19)
C(33)	5630(29)	188(27)	8433(23)
O(33)	5942(24)	−521(22)	8249(18)
C(41)	3141(27)	65(24)	8833(22)
O(41)	3037(20)	−106(18)	9557(16)
C(42)	2613(32)	−1382(30)	6976(25)
O(42)	2688(22)	−2254(21)	6654(17)
C(43)	1730(31)	−107(28)	6270(25)
O(43)	971(23)	−392(20)	5503(18)
C(1A)	3398(25)	4890(22)	5947(19)
C(1B)	3547(30)	5203(27)	5194(24)
C(1C)	4496(36)	6293(32)	5382(29)
C(1D)	5331(35)	7062(32)	6255(27)
C(1E)	5291(32)	6779(29)	7014(25)
C(1F)	4307(32)	5701(29)	6881(26)
C(2A)	926(25)	3833(23)	6058(19)
C(2B)	836(37)	4826(33)	6045(27)
C(2C)	−262(30)	4942(29)	6138(23)
C(2D)	−1198(37)	4043(32)	6234(27)
C(2E)	−1075(44)	3103(39)	6307(32)
C(2F)	−29(35)	3023(32)	6230(26)
C(3A)	−300(30)	−280(27)	7933(23)
C(3B)	163(41)	346(36)	8954(32)
C(3C)	−321(35)	1112(32)	9266(29)
C(3D)	−972(37)	1413(35)	8678(30)
C(3E)	−1305(31)	944(28)	7725(25)
C(3F)	−954(35)	82(32)	7341(29)

Table 8 (continued)

	x	*y*	*z*
C(4A)	−96(26)	−2285(23)	7972(20)
C(4B)	−1278(34)	−2742(30)	7997(25)
C(4C)	−1609(36)	−3621(30)	8360(26)
C(4D)	−779(34)	−3937(31)	8728(27)
C(4E)	446(35)	−3532(31)	8608(26)
C(4F)	790(33)	−2639(28)	8244(24)

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