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CLUSTER CHEMISTRY. SYNTHESIS AND X-RAY STRUCTURE OF $Os_5(\mu_5$-η^2,P-$C_2PPh_2)(\mu$-$PPh_2)(CO)_{13}$, A COMPLEX CONTAINING A PHOSPHINO-ALKYNE LIGAND ATTACHED TO AN OPEN Os_5 CLUSTER

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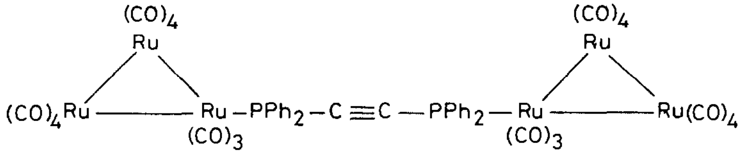
Summary

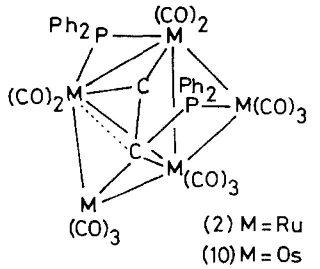
Reaction of $C_2(PPh_2)_2$(dppa) with $Os_3(CO)_{11}(NCMe)$ affords the yellow complex $[Os_3(CO)_{11}]_2(\mu$-dppa); this on heating gives $[Os_5(\mu_5$-η^2-P-$C_2PPh_2)(\mu$-$PPh_2)(CO)_{13}]$ in 51% yield, which is shown by an X-ray study to contain a seven electron donor C_2PPh_2 ligand interacting with all five Os_5 atoms of an open Os_5 cluster consisting of three edge fused Os_3 triangles with a "swallowlike" arrangement. The PPh_2 group bridges the non fused edge of the central triangle. The structure appears to be identical with that described for the equivalent ruthenium complex.

Introduction

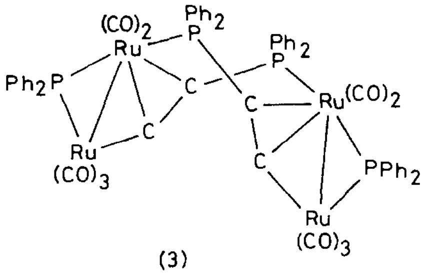
We recently described the radical anion-induced synthesis of the bis-trinuclear cluster complex $\{Ru_3(CO)_{11}\}_2(\mu$-dppa) (**1**,dppa = $C_2(PPh_2)_2$) and its thermal condensation to the pentanuclear $Ru_5(\mu_5$-η^2,P-$C_2PPh_2)(\mu$-$PPh_2)(CO)_{13}$ (**2**) in 88% yield [1]. In the formation of **2**, cleavage of a P–C(*sp*) bond in the dppa ligand has given a μ-PPh_2 group which bridges one edge of the cluster, and a diphenylphosphinoethynyl ligand. This is attached to all five metal atoms: the C_2 fragment interacts with four rutheniums, while the phosphorus atom bonds to the fifth by a conventional 2e donor bond. The thermal reaction between $Ru_3(CO)_{12}$ and dppa also gives **2**, in 28% yield [2], together with $Ru_4(\mu_3$-η^2,P-$C_2PPh_2)_2(\mu$-$PPh_2)_2$-$(CO)_{10}$ (**3**) and, under different conditions, $Ru_4(\mu_4$-PPh$)(\mu_4$-$PhC_2PPh_2)(CO)_{10}$ (**4**) [3]. Not surprisingly, the extended interaction of the C ··· C bond in **2** renders it susceptible to further reaction: successive addition of three molecules of H_2 affords



(1)



(2) M = Ru
(10) M = Os



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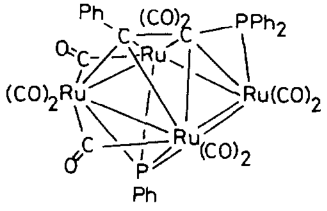

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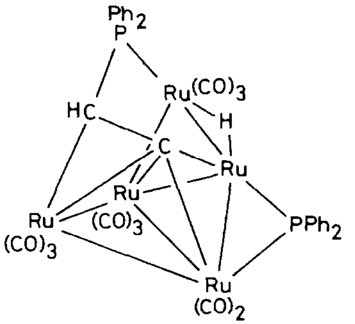
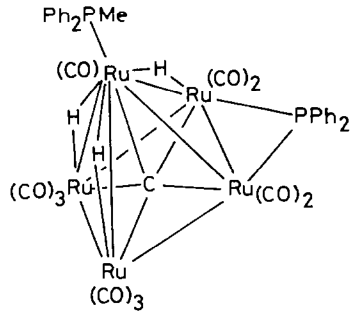


(5)

in a stepwise fashion the pentanuclear complexes $Ru_5(\mu\text{-}H)(\mu_5\text{-}\eta^2\text{-}P\text{-}C{=}CHPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**5**), $Ru_5(\mu\text{-}H)_2(\mu_5\text{-}\eta^2\text{-}P\text{-}CCH_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**6**) and $Ru_5C(\mu\text{-}H)_3(\mu\text{-}PPh_2)(CO)_{11}(PMePh_2)$ (**7**) [4]. Carbonylation gave two isomers of a pentanuclear $(CO)_{15}$ complex [5], one of which under more vigorous conditions undergoes cleavage of the second P–C(*sp*) bond to give $Ru_4(\mu_4\text{-}\eta^2\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{12}$ (**8**) [6]. The extensive skeletal changes and chemistry of the acetylenic moiety in these complexes suggested that a study of the analogous osmium system would also yield some interesting results: herein, we report the synthesis and X-ray structure of the osmium analogue of **2**.

Results and discussion

In contrast to those of $Ru_3(CO)_{12}$, reactions between $Os_3(CO)_{12}$ and tertiary phosphines in the presence of sodium diphenylketyl result in polysubstitution and generally have no advantages over thermal reactions [7,8]. However, complexes of



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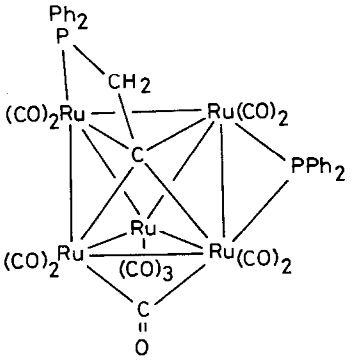

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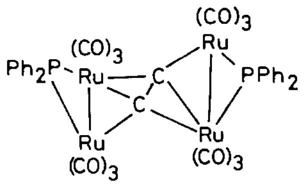

(8)

the type $Os_3(CO)_{11}(L)$ ($L = CO$, PPh_3, $4\text{-}CH_3C_6H_4SO_2CH_2NC$) have been prepared quantitatively from the reaction of $Os_3(CO)_{11}(NCMe)$ with the appropriate ligand L [9]. Treatment of $Os_3(CO)_{11}(NCMe)$ with dppa in a 2/1 ratio at ambient temperature similarly afforded $\{Os_3(CO)_{11}\}_2(\mu\text{-dppa})$ (**9**) in 87% yield. This yellow complex was identified by the usual methods, its spectroscopic properties being similar to those of **1** [1]. Thus, the IR $\nu(CO)$ spectrum contained nine absorptions between 2092–1968 cm^{-1}; the ^1H NMR spectrum was featureless apart from the aromatic multiplet at δ 7.42.

On heating in refluxing xylene, the yellow solution of **9** slowly darkened, and after 2.5 h, TLC showed that no **9** remained. Isolation by preparative TLC afforded a purple powder of $Os_5(\mu_5\text{-}\eta^2\text{-}P\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**10**), which was characterised by microanalysis and from its spectral properties, which were generally similar to those of **2** ($M = Ru$). The identity of the osmium complex has been fully confirmed by the single-crystal X-ray study described below.

A molecule of **10** is shown in Fig. 1. As predicted from spectral studies and preliminary X-ray investigations, the molecular structures of complexes **10** ($M = Os$) and **2** ($M = Ru$) are identical. The five Os atoms form an open array of three edge-fused triangles in a "swallowlike" arrangement with two dihedral angles of 134.9 and 153.2° along Os(1)-Os(3) and Os(2)-Os(3) edges, respectively (similar values, 134.3 and 152.4°, were observed in the Ru complex). The C_2PPh_2 group, formed by cleavage of PPh_2 from the original dppa ligand, interacts with all five metal atoms. The alkyne unit, C(1)–C(2), is strongly σ-bonded to Os(1), Os(2) and

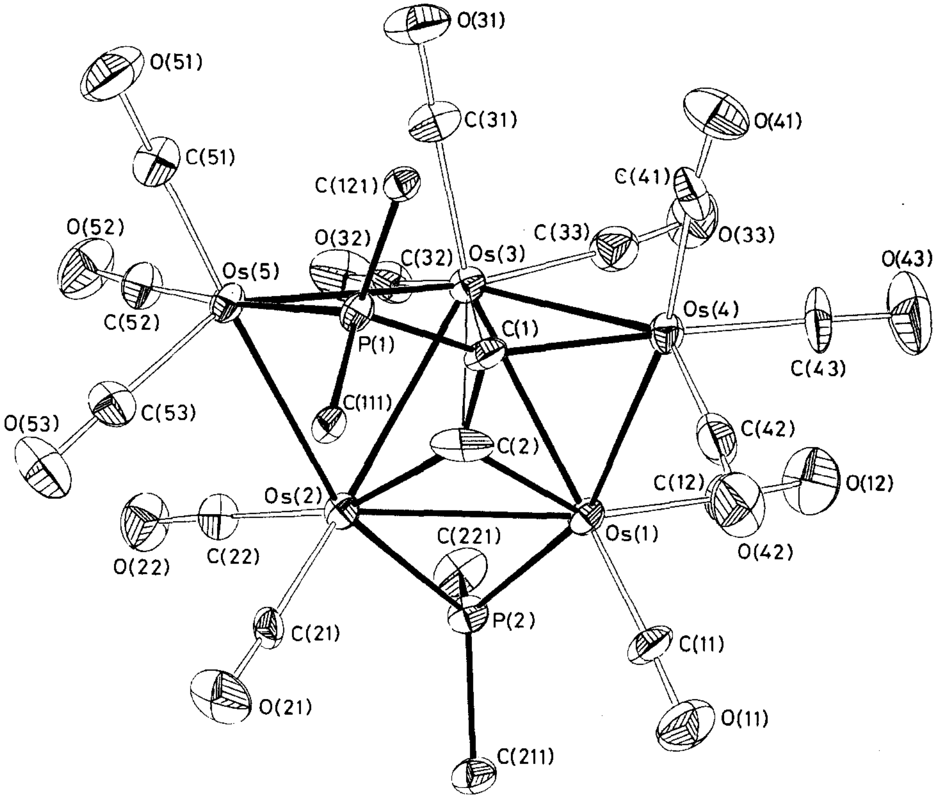

Fig. 1. ORTEP view of the molecular structure of **10**. Carbon atoms of phenyl rings have been omitted for clarity. Ellipsoids represent 30% probability.

TABLE 1

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (deg.) IN THE HEAVY-ATOM CORES OF COMPLEXES **2**(M = Os, Ru) (E.s.d.'s in parentheses refer to the last significant digit)

	M = Os	M = Ru	
		Ref. 2	Ref. 1
M(1)-M(2)	2.7420(7)	2.723(2)	2.731(2)
M(1)-M(3)	2.9344(7)	2.906(2)	2.909(1)
M(1)-M(4)	2.8775(7)	2.853(2)	2.854(2)
M(2)-M(3)	2.9217(7)	2.889(2)	2.890(1)
M(2)-M(5)	2.9128(7)	2.929(2)	2.932(2)
M(3)-M(4)	2.8952(7)	2.847(2)	2.848(1)
M(3)-M(5)	2.9252(7)	2.913(2)	2.921(2)
M(1)-C(2)	2.04(1)	2.04(2)	2.024(5)
M(2)-C(2)	2.01(2)	2.01(2)	2.016(5)
C(1)-C(2)	1.38(2)	1.38(2)	1.383(6)
M(4)-C(1)	2.05(1)	2.03(2)	2.055(5)
M(3)-C(1)	2.27(1)	2.29(2)	2.279(4)
M(3)-C(2)	2.19(1)	2.16(2)	2.154(4)
P(1)-C(1)	1.78(1)	1.77(2)	1.762(5)
M(5)-P(1)	2.389(3)	2.376(5)	2.373(2)
M(1)-P(2)	2.286(3)	2.276(5)	2.279(2)
M(2)-P(2)	2.358(3)	2.342(5)	2.353(2)

Os(4), and shows an asymmetric η^2 interaction with Os(3). The link to the fifth metal atom Os(5) involves a conventional two-electron donor interaction of the phosphorus atom P(1) still attached to the alkyne. In keeping with the observations for the Ru complex **2**, the Os(1), Os(2), Os(4), C(1), C(2) and P(1) are roughly in the same plane, the largest deviation from this plane being 0.18 Å for the phosphorus atom P(1). Table 1 shows the heavy atom cores of the two complexes together with the diphenylphosphinoethynyl interactions with the M_5 skeletons. There is not much difference between them; the metal–metal and metal–ligand interactions fall in the same range. However, it is worth to point out that of the seven Os–Os separations, five are significantly longer than the corresponding Ru–Ru distances (0.019 to 0.047 Å) owing to the difference in the covalent radii of Os and Ru while bonds from Os(5), which bears the phosphine donor atom, to Os(2) and Os(3), are identical within experimental error in both complexes. As was suggested for the Ru compound **2** [1], this may be related to the presence of the tertiary phosphine ligand, which simultaneously constrains Os(5) and lengthens the bonds to the rest of the cluster.

Experimental

The experimental conditions were similar to those employed in the synthesis and characterisation of the ruthenium analogues [1]. Dppa was obtained from Strem Chemicals Inc., Newburyport, MA 01950; $Os_3(CO)_{11}(NCMe)$ was prepared by a published method [9].

Preparation of $[Os_3(CO)_{11}]_2(\mu\text{-dppa})$ (9)

A mixture of $Os_3(CO)_{11}(NCMe)$ (152 mg, 0.165 mmol), MeCN (5 ml) and dppa (33 mg, 0.083 mmol) in cyclohexane (100 ml) was stirred at 50°C for 30 min. Evaporation and recrystallisation from CH_2Cl_2/MeOH afforded yellow crystals of $\{Os_3(CO)_{11}\}_2(\mu\text{-dppa})$ (**9**) (155 mg, 87%), m.p. 189–190°C. [Found: C, 26.81; H, 0.60; $C_{48}H_{20}O_{22}Os_6P_2$ calc: C, 26.79; H, 0.94%]. Infrared (cyclohexane): ν(CO) 2112s, 2062m, 2040w, 2026s, 2008w, 1999w, 1989w cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 7.45 (m, Ph).

Pyrolysis of $[Os_3(CO)_{11}]_2(\mu\text{-dppa})$ (9)

A solution of $[Os_3(CO)_{11}]_2(\mu\text{-dppa})$ (**9**) (65 mg, 0,030 mmol) in xylene (50 ml) was gently refluxed for 2.5 h, after which the reaction was adjudged complete (TLC). Evaporation and preparative TLC (petroleum spirit/acetone 80/20) gave one major purple band, R_f 0.30, and recrystallisation of the solid isolated from this band from CH_2Cl_2/MeOH gave, as a purple powder, $Os_5(\mu_5\text{-}\eta^2\text{-}P\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**10**) (26 mg, 51%), m.p. > 200°C. [Found: C, 27.27; H, 0.98; $C_{39}H_{20}O_{13}Os_5P_2$ calc: C, 27.40; H, 1.18%]. Infrared (cyclohexane): ν(CO) 2092m, 2070s, 2062s, 2040w, 2021vs, 2004w, 1994w, 1978w, 1968w cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 7.42 (m, Ph).

Crystallography

Crystal data. $C_{39}H_{20}O_{13}P_2Os_5$, $M = 1709.5$, monoclinic, space group $P2_1/n$, a 14.239(4), b 17.316(3), c 16.972(5) Å, β 92.47(2)°, V 4181(4) Å^3, D_m 2.70(1), D_c 2.72 g cm^{-3} for $Z = 4$, λ(Mo-K_α) 0.71069, μ(Mo-K_α) 162.4 cm^{-1}. Specimen: 0.15 ×

TABLE 2

FRACTIONAL ATOMIC COORDINATES AND U_{eq} (with e.s.d.'s in parentheses)

Atom	x	y	z	U [a]
Os(1)	0.22140(3)	0.24245(3)	0.24184(3)	0.0275
C(11)	0.203(1)	0.3395(8)	0.2805(8)	0.0391
O(11)	0.195(1)	0.4024(7)	0.3033(8)	0.0733
C(12)	0.161(1)	0.1993(9)	0.3262(8)	0.0383
O(12)	0.125(1)	0.1702(9)	0.3785(9)	0.0801
P(2)	0.1043(2)	0.2427(2)	0.1454(2)	0.0295
C(1)	0.4276(8)	0.2294(7)	0.2067(8)	0.0286
C(2)	0.339(1)	0.2474(6)	0.1771(9)	0.0304
Os(2)	0.24910(3)	0.23904(3)	0.08299(3)	0.0265
C(21)	0.2600(9)	0.3354(8)	0.0352(7)	0.0237
O(21)	0.2687(8)	0.3934(6)	0.0055(8)	0.0596
C(22)	0.1884(9)	0.1973(8)	−0.0078(8)	0.0334
O(22)	0.1470(7)	0.1725(6)	−0.0622(6)	0.0573
Os(3)	0.34262(3)	0.12104(3)	0.18122(3)	0.0270
C(31)	0.4436(9)	0.0491(8)	0.1744(8)	0.0360
O(31)	0.4975(8)	0.0011(6)	0.1710(7)	0.0630
C(32)	0.259(1)	0.0619(8)	0.1178(8)	0.0343
O(32)	0.2075(7)	0.0227(6)	0.0783(7)	0.0493
C(33)	0.298(1)	0.075(1)	0.275(1)	0.0461
O(33)	0.264(1)	0.0348(8)	0.3199(9)	0.0612
Os(4)	0.39838(3)	0.20697(3)	0.32190(3)	0.0305
C(41)	0.517(1)	0.1692(8)	0.3575(8)	0.0452
O(41)	0.5882(8)	0.1486(7)	0.3835(7)	0.0634
C(42)	0.416(1)	0.3085(9)	0.3582(8)	0.0362
O(42)	0.430(1)	0.3709(7)	0.3732(7)	0.0702
C(43)	0.342(1)	0.173(1)	0.4153(9)	0.0479
O(43)	0.309(1)	0.152(1)	0.4710(8)	0.0822
Os(5)	0.42271(3)	0.16890(3)	0.03306(3)	0.0287
C(51)	0.5283(9)	0.1145(9)	0.0029(9)	0.0424
O(51)	0.5920(9)	0.0795(9)	−0.0185(8)	0.0770
C(52)	0.3482(9)	0.1033(8)	−0.0345(7)	0.0366
O(52)	0.3090(8)	0.0629(7)	−0.0776(7)	0.0639
C(53)	0.4315(9)	0.2481(8)	−0.0427(9)	0.0390
O(53)	0.4311(9)	0.2954(8)	−0.0889(7)	0.0685
P(1)	0.5114(2)	0.2387(2)	0.1323(2)	0.0276
C(111)	0.5319(9)	0.3415(7)	0.1165(7)	0.0309
C(112)	0.612(1)	0.3637(9)	0.0769(9)	0.0454
C(113)	0.624(1)	0.441(1)	0.061(1)	0.0580
C(114)	0.564(1)	0.4957(9)	0.086(1)	0.0560
C(115)	0.489(1)	0.4736(8)	0.126(1)	0.0578
C(116)	0.471(1)	0.3968(8)	0.1430(9)	0.0442
C(121)	0.6217(8)	0.2064(7)	0.1784(8)	0.0308
C(122)	0.658(1)	0.1330(9)	0.1686(9)	0.0492
C(123)	0.737(1)	0.108(1)	0.210(1)	0.0547
C(124)	0.782(1)	0.156(1)	0.264(1)	0.0547
C(125)	0.750(1)	0.227(1)	0.275(1)	0.0537
C(126)	0.669(1)	0.2539(9)	0.2341(9)	0.0506
C(211)	0.0251(9)	0.3248(7)	0.1369(8)	0.0367
C(212)	0.053(1)	0.394(1)	0.108(1)	0.0652
C(213)	−0.007(2)	0.456(1)	0.106(1)	0.0750
C(214)	−0.093(1)	0.451(1)	0.135(1)	0.0689
C(215)	−0.121(1)	0.383(1)	0.161(2)	0.0746
C(216)	−0.062(1)	0.320(1)	0.165(1)	0.0680

TABLE 2 (continued)

Atom	x	y	z	U ^{a}
C(221)	0.0269(9)	0.1600(8)	0.1287(9)	0.0349
C(222)	−0.036(1)	0.157(1)	0.0663(9)	0.0535
C(223)	−0.091(2)	0.093(2)	0.053(1)	0.0737
C(224)	−0.082(1)	0.030(1)	0.100(1)	0.0660
C(225)	−0.023(1)	0.0326(9)	0.163(1)	0.0627
C(226)	0.033(1)	0.0972(9)	0.179(1)	0.0529

^{a} $u_{eq} = (U_1 \star U_2 \star U_3)^{1/3}$

0.12 × 0.10 mm. Data: 6669 reflexions were collected in the range $3 < 2\theta < 46°$ on an Enraf–Nonius CAD-4 diffractometer; the 4055 merged reflexions with $I > 2\sigma(I)$ were used in subsequent calculations. Empirical absorption correction was applied [10].

Structural determination. The structure was solved by direct methods (MULTAN [11]) to give the osmium atom positions. All remaining non-hydrogen atoms were found by successive electron density maps calculations. The hydrogen atoms were given calculated positions (C–H, 0.98 Å) with a fixed overall isotropic thermal parameter. Coordinates of these H atoms were not refined, but recalculated after each cycle. The structure was refined by least-squares techniques (with all non-hydrogen atoms anisotropic) with a large-block approximation to the normal matrix, to $R = 0.0309$, $R_w = 0.0373$ where $w = w'[1 - \{(F_o - F_c/6\sigma(F_o))\}^2]^2$ with $w' = 1/\Sigma^n_{r=1} A_r T_r(X)$ with 3 coefficients, A_r, 3.080, −0.593, 2.157, for the Chebyshev polynomial $T_r(X)$ where X was $F_c/F_c(\text{max})$ [12]. (CRYSTALS [13]). The criteria for a satisfactory completed analysis was the value of the rms(shift/esd) equal to 0.09, and no significant features in the final difference map.

The atomic coordinates are listed in Table 2. A full list of bond lengths and angles, and lists of calculated and observed structure factors and thermal parameters are available from the authors.

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