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XXXVI*. HYDROGENATION OF AN OPEN Ru_5 CLUSTER: EXCISSION OF A RUTHENIUM CARBONYL FRAGMENT. X-RAY STRUCTURE OF $Ru_4(\mu\text{-}H)_3(\mu_4\text{-}\eta^2,P\text{-}HC_2PPh_2)(\mu\text{-}PPh_2)(CO)_{10}$

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Summary

Hydrogenation (25°C, 10 atm) of $Ru_5(\mu_5\text{-}\eta^2,P\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ gave $Ru_4(\mu\text{-}H)_4(CO)_{12}$ and the tetranuclear $Ru_4(\mu\text{-}H)_3(\mu_4\text{-}\eta^2,P\text{-}HC_2PPh_2)(\mu\text{-}PPh_2)(CO)_{10}$; an X-ray structure shows the presence of a $HC{\equiv}CPPh_2$ ligand bonded to all four atoms of a metallo-ligated triangular cluster.

We have described the open Ru_5 cluster $Ru_5(\mu_5\text{-}\eta^2,P\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (1) [1], and others have recently reported [2] the synthesis of the related complex $Ru_5(\mu_5\text{-}\eta^2\text{-}C_2Ph)(\mu_3\text{-}\eta^2\text{-}PhC_2C_2Ph)(\mu\text{-}PPh_2)(CO)_{12}$, in both of which the acetylide unit is wrapped around by the five metal atoms. The ready availability of 1, which is obtained in >80% yield by heating $[Ru_3(CO)_{11}]_2\{\mu\text{-}(Ph_2P)_2C_2\}$, provided an opportunity to examine its reactions with small molecules. Herein we report some initial results of a study of the reaction of H_2 with 1.

Under 10 atm H_2, complex 1 afforded the tetranuclear complex 2 in 61% yield; the fifth ruthenium is partially recovered as $Ru_4(\mu\text{-}H)_4(CO)_{12}$ (15%). A single crystal X-ray study of 2 was carried out to determine its molecular structure.

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[*] For Part XXXV, see ref. 10.

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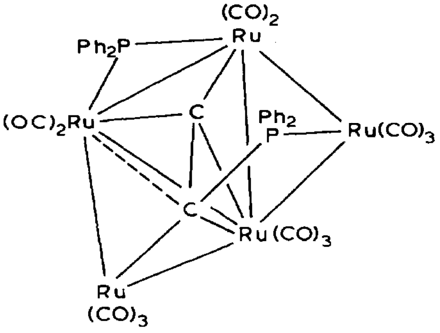
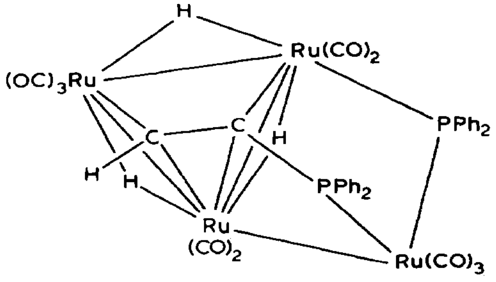


(1)



(2)

Crystal data 2: $Ru_4(\mu\text{-}H)_3(\mu_4\text{-}\eta^2,P\text{-}HC_2PPh_2)(\mu\text{-}PPh_2)(CO)_{10} \equiv C_{36}H_{24}O_{10}P_2Ru_4$, M = 1082.8. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a 13.280(3), b 12.535(3), c 11.583(2) Å, α 86.54(2), β 86.47(2), γ 81.45(2)°, U 1900.6(7) Å^3. D_c (Z = 2) 1.89 g cm^{-3}. $F(000)$ = 1052. Monochromatic Mo-K_α radiation, λ 0.71069 Å, μ 15.6 cm^{-1}. Specimen: 0.30 × 0.50 × 0.30 mm. $A^*_{\min,\max}$ = 1.47; 1.71 T 295 K.

Structure determination. A unique data set was measured to the limit $2\theta_{\max}$ 65°, using a Syntex P2$_1$ four-circle diffractometer to conventional $2\theta/\theta$ scan mode. 12670 independent reflections were obtained, 10070 with $I > 3\sigma(I)$ being considered "observed" and used in the basically 9 × 9 block diagonal least squares refinement after Gaussian absorption correction and solution of the structure by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{\text{iso}})_H$ were refined also. At convergence, residuals were 0.028 (R), 0.036 (R', statistical weights). Neutral complex scattering factors were used [3]; computation used the XTAL 83 program system implemented on a Perkin—Elmer 3240 computer by S.R. Hall. Non-hydrogen atom numbering is shown in the Figure; non-hydrogen atom coordinates are given in Table 1*.

Figure 1 shows an ORTEP plot of one molecule of 2, and Table 2 details the core geometry. The complex consists of a triangular Ru$_3$ core, to which is attached the fourth ruthenium in an equatorial position. The four metal atoms are not coplanar (Ru(4) being out of the plane of the other three by 1.041 Å), and all achieve an 18*e* configuration. The C_2PPh_2 moiety in 1 has been converted to an ethynyldiphenylphosphine ligand, which is attached to all four metal atoms via a normal 2*e* donor bond from P(4) to Ru(4), and the C_2 system interacting with the Ru$_3$ triangle in the common $\mu_3\text{-}2\eta^1,\eta^2$ mode. The μ-PPh$_2$ group, originally bridging an Ru—Ru bond in 1, now bridges Ru(2) and Ru(4) which are not within bonding distance of each other. The ten CO groups are distributed two each to Ru(1) and Ru(2), and three each to Ru(3) and Ru(4). The hydride ligands were located and refined in the

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*Tables of carbonyl geometries, ligand hydrogen atom parameters and phenyl ring geometries are included in supplementary material. These may be obtained from the Director, Cambridge Crystallographic Data Centre, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW, England. The full literature citation for this Communication should accompany any request.

TABLE 1

NON-HYDROGEN ATOM COORDINATES
(Core hydrogen atoms are included, however)

Atom	*x*	*y*	*z*
Ru(1)	0.11109(2)	0.33064(2)	0.35939(2)
Ru(2)	0.30943(2)	0.27466(2)	0.44477(2)
Ru(3)	0.13898(2)	0.16548(2)	0.56711(2)
Ru(4)	0.22073(2)	0.35888(2)	0.14423(2)
H(12)	0.201(2)	0.363(2)	0.441(2)
H(13)	0.071(2)	0.290(2)	0.511(2)
H(23)	0.261(2)	0.207(3)	0.558(3)
C(11)	0.0358(3)	0.4408(3)	0.3560(3)
O(11)	—0.0124(3)	0.5235(2)	0.3555(3)
C(12)	0.0019(2)	0.2460(3)	0.2980(3)
O(12)	—0.0657(2)	0.2110(3)	0.2668(3)
C(21)	0.3389(3)	0.3741(3)	0.5543(3)
O(21)	0.3521(3)	0.4301(2)	0.6226(3)
C(22)	0.4351(2)	0.1837(2)	0.4649(3)
O(22)	0.5085(2)	0.1277(2)	0.4826(2)
C(31)	0.2053(3)	0.0262(3)	0.6211(3)
O(31)	0.2413(2)	—0.0570(2)	0.6462(3)
C(32)	0.0070(3)	0.1229(3)	0.5728(3)
O(32)	—0.0719(2)	0.0993(2)	0.5724(3)
C(33)	0.1197(3)	0.2401(3)	0.7144(3)
O(33)	0.1134(3)	0.2843(3)	0.7965(2)
C(41)	0.2911(3)	0.3653(3)	—0.0046(3)
O(41)	0.3234(2)	0.3670(3)	—0.0981(2)
C(42)	0.0916(2)	0.3422(3)	0.0843(2)
O(42)	0.0153(2)	0.3396(2)	0.0483(2)
C(43)	0.1759(3)	0.5135(3)	0.1450(3)
O(43)	0.1502(2)	0.6030(2)	0.1401(3)
P(2)	0.35226(5)	0.38261(5)	0.27800(6)
C(211)	0.4863(2)	0.3612(2)	0.2219(2)
C(212)	0.5140(3)	0.3796(3)	0.1059(3)
C(213)	0.6157(3)	0.3662(3)	0.0669(3)
C(214)	0.6910(3)	0.3356(3)	0.1418(4)
C(215)	0.6652(3)	0.3200(3)	0.2572(4)
C(216)	0.5644(3)	0.3327(3)	0.2973(3)
C(221)	0.3421(2)	0.5267(2)	0.3155(3)
C(222)	0.2610(3)	0.5729(3)	0.3865(3)
C(223)	0.2535(3)	0.6784(3)	0.4180(4)
C(224)	0.3266(4)	0.7402(3)	0.3784(4)
C(225)	0.4044(4)	0.6983(3)	0.3078(5)
C(226)	0.4140(3)	0.5904(3)	0.2750(4)
P(4)	0.27425(5)	0.17187(5)	0.18767(5)
C(411)	0.2115(2)	0.0707(2)	0.1243(2)
C(412)	0.2184(2)	—0.0339(2)	0.1755(3)
C(413)	0.1785(3)	—0.1134(3)	0.1226(4)
C(414)	0.1329(3)	—0.0914(3)	0.0194(4)
C(415)	0.1259(3)	0.0104(3)	—0.0320(3)
C(416)	0.1652(2)	0.0916(3)	0.0202(2)
C(421)	0.4075(2)	0.1111(2)	0.1695(2)
C(422)	0.4475(2)	0.0316(3)	0.2504(3)
C(423)	0.5468(3)	—0.0191(4)	0.2348(3)
C(424)	0.6069(3)	0.0099(4)	0.1417(4)
C(425)	0.5702(3)	0.0852(4)	0.0638(4)
C(426)	0.4688(3)	0.1379(3)	0.0746(3)
C(431)	0.2469(2)	0.1709(2)	0.3411(2)
C(432)	0.1693(2)	0.1238(2)	0.3969(2)
H(432)	0.132(2)	0.076(2)	0.361(2)

TABLE 2

CORE GEOMETRY

(The first column in each matrix is the ruthenium—other atom distance (Å). Other entries are the angles (degrees) subtended at the ruthenium atom by the relevant atoms at the head of the row and column.)

Ru(1)	*r*	Ru(3)	Ru(4)	C(11)	C(12)	C(431)	C(432)
Ru(2)	2.8370(6)	64.61(1)	82.19(2)	117.48(12)	152.05(10)	47.33(6)	69.39(7)
Ru(3)	2.8683(5)		140.96(1)	123.44(10)	100.83(10)	68.01(6)	45.74(6)
Ru(4)	2.9178(5)			89.16(10)	99.57(9)	74.55(6)	104.91(6)
C(11)	1.888(3)				90.5(2)	158.4(1)	165.4(1)
C(12)	1.887(4)					105.9(1)	83.4(1)
C(431)	2.251(2)						35.37(9)
C(432)	2.261(2)						

Ru(2)	*r*	Ru(3)	P(2)	C(21)	C(22)	C(431)
Ru(1)	2.8370(6)	58.19(2)	85.66(2)	118.73(10)	147.58(9)	51.60(6)
Ru(3)	3.0490(5)		143.77(2)	104.12(10)	108.65(9)	65.70(6)
P(2)	2.3799(7)			95.02(10)	100.77(9)	90.91(7)
C(21)	1.927(4)				92.5(1)	168.3(1)
C(22)	1.895(3)					96.3(1)
C(431)	2.112(3)					

Ru(3)	*r*	Ru(2)	C(31)	C(32)	C(33)	C(432)
Ru(1)	2.8683(5)	57.20(1)	141.24(10)	95.10(10)	116.16(10)	51.47(7)
Ru(2)	3.0490(5)		104.63(11)	151.84(10)	100.82(12)	66.98(8)
C(31)	1.922(3)			94.3(1)	100.1(1)	90.6(1)
C(32)	1.903(4)				96.1(2)	92.6(1)
C(33)	1.980(3)					165.7(1)
C(432)	2.071(2)					

Ru(4)	*r*	P(4)	P(2)	C(41)	C(42)	C(43)
Ru(1)	2.9178(5)	72.82(2)	82.39(2)	167.48(12)	80.32(8)	96.93(9)
P(4)	2.3790(8)		83.56(3)	96.43(10)	96.16(10)	167.57(10)
P(2)	2.4665(8)			103.14(11)	161.96(9)	88.18(10)
C(41)	1.912(3)				94.8(1)	94.5(1)
C(42)	1.933(3)					88.8(1)
C(43)	1.941(3)					

For H(12), Ru(1,2)—H(12), 1.86(3), 1.68(2) Å; Ru(1)—H—Ru(2), 106(1)°. For H(13), Ru(1,3)—H(13), 1.81(3) 1.78(3) Å; Ru(1)—H—Ru(3), 106(1)°. For H(23), Ru(2,3)—H(23), 1.67(3), 1.77(3) Å; Ru(2)—H—Ru(3), 125(2)°. For H(432), C(432)—H(432), 0.97(3) Å; H(432)—C(432)—Ru(1,3), C(431), 114(2), 123(2), 123(2)°.

P(2)	*r*	Ru(4)	C(211)	C(221)
Ru(2)	2.3799(7)	102.62(3)	116.87(9)	109.87(9)
Ru(4)	2.4665(8)		117.41(10)	110.96(10)
C(211)	1.844(3)			99.2(1)
C(221)	1.866(3)			

P(4)	*r*	C(411)	C(421)	C(431)
Ru(4)	2.3790(8)	119.99(8)	121.89(9)	98.16(7)
C(411)	1.828(3)		100.6(1)	110.1(1)
C(421)	1.824(3)			105.1(1)
C(431)	1.791(2)			

C(431)—C(432), 1.371(4) Å; P(4)—C(431)—Ru(1,2), C(432), 102.9(1), 121.0(1), 124.0(2)°. C(431)—C(432)—Ru(1,3), 71.9(1), 113.8(2)°.

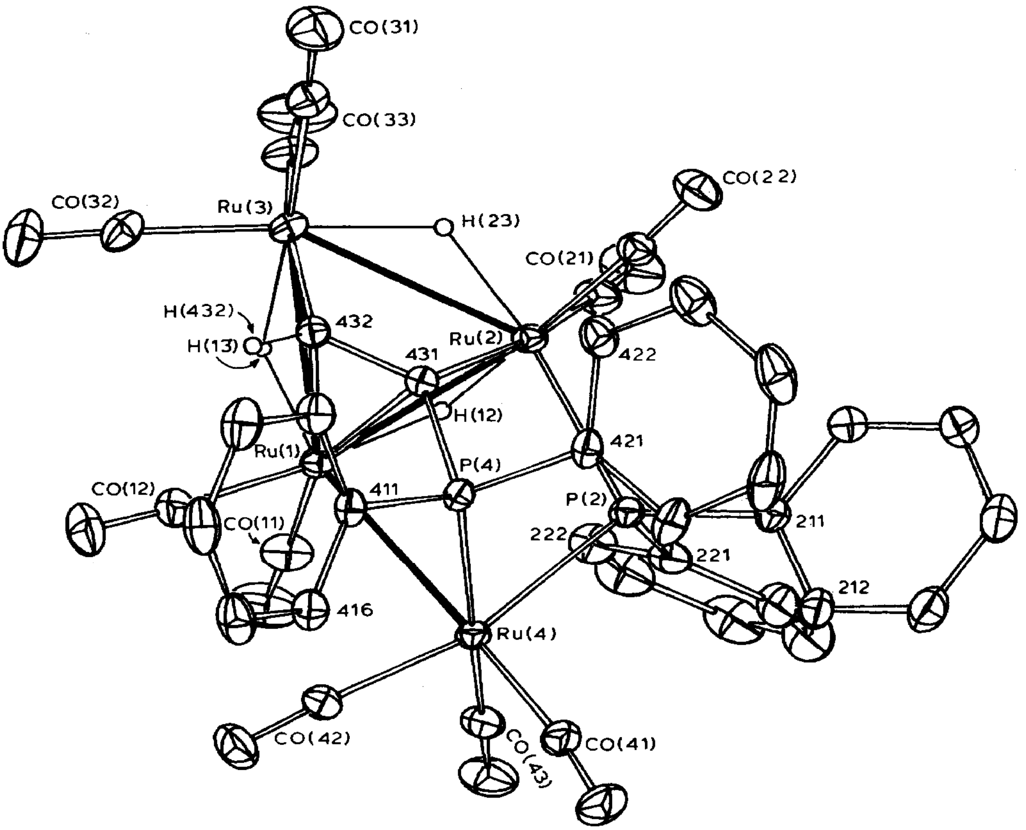
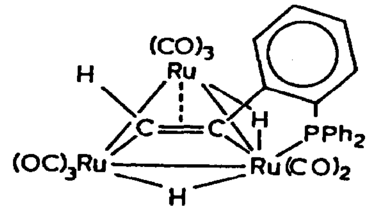


Fig. 1. ORTEP plot of one molecule of $Ru_4(\mu\text{-}H)_3(\mu_4\text{-}\eta^2,P\text{-}HC_2PPh_2)(\mu\text{-}PPh_2)(CO)_{10}$ (2), showing atom numbering scheme, and 20% thermal ellipsoids for the non-hydrogen atoms. Hydrogen atoms associated with the cluster are shown with arbitrary radii 0.1 Å. Metal—metal bonds are shown as solids, bonds to the cluster hydrogens as single lines.

structure determination, and bridge the three edges of the Ru_3 triangle; observation of three resonances in the ^1H NMR spectrum of 3 shows that they are not fluxional at room temperature.



(3)

The shortest metal—metal bond is Ru(1)—Ru(2) (2.8370(6) Å), and although similar to a bond of length 2.874(1) Å in $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\eta^2, P\text{-}HC_2C_6H_4PPh_2)(CO)_8$ (3) [4], it is additionally "bridged" by the Ru(4)P(2) moiety. The Ru(1)—Ru(3) (2.8683(5) Å) and Ru(2)—Ru(3) bonds (3.0490(5)

Å) resemble more closely the similar bonds found in 3 (2.874(1) and 3.021(1) Å, respectively). The relatively long Ru(1)—Ru(4) bond (2.9178(5) Å) probably results from the steric problems in coordinating two PPh_2 groups in mutually *cis*-positions (angle P(2)Ru(4)P(4) 83.56(3)°) while still remaining attached to the cluster.

The acetylenic CC bond undergoes the usual lengthening to 1.371(4) Å upon coordination to the Ru_3 core, but it is not as long as those found in $Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)(\mu\text{-}PPh_2)(CO)_9$ (1.415(11) Å [2] or 3 (1.44(3) Å) [2]. The Ru—P distances (Ru(2)—P(2) 2.3799(7), Ru(4)—P(4) 2.3790(8), Ru(4)—P(2) 2.4665(8) Å) are consistent with 2*e* donor bonds in the first two cases, and with a phosphido—metal bond from P(2) to Ru(4), as required by the 18*e* counts.

Tetrametal clusters usually have 60*e* (tetrahedral, six metal—metal bonds), 62*e* (butterfly, five metal—metal bonds) or 64*e* (planar rhomboidal, five metal—metal bonds) electron counts. Some lengthening (and weakening) of the metal—metal separations is usually evident in the latter, electron-rich, clusters [5,6]. Complex 2 provides an example of a 64*e* cluster in which cleavage of a metal—metal bond, expected on addition of a 2*e* ligand to a 62*e* butterfly cluster, has occurred. The Ru(2)...Ru(4) separation is 3.7831(6) Å, while the average bonded Ru—Ru separation is 2.918 Å. This value is considerably longer than found in $Ru_4(\mu_4\text{-C=CHPr}^i)(\mu_3\text{-OR})(\mu\text{-}PPh_2)(CO)_{10}$ (R = H, Et), which also have 64*e*, where the hinge of the butterfly has cleaved; the average Ru—Ru distances in these complexes are 2.766 (R = H) and 2.758 Å (R = Et) [7].

The mechanism of formation of 2 cannot be proposed with certainty at this stage. A reasonable site for initial attack is the Ru(3)—C(1) bond in 1; addition of H_2 and cleavage of the PPh_2 bridge would allow elimination of an $HRu(CO)_3$ fragment (which appears as $Ru_4(\mu\text{-H})_4(CO)_{12}$). The final $\mu\text{-}2\eta^1,\eta^2$ geometry found for the alkyne must result from a rotation about the Ru_3 core, perhaps similar to that which relates the two isomers of $OsW_2\{\mu_3\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_7(\eta\text{-}C_5H_5)_2$ [8,9]. The net reaction is:

$$4Ru_5(\mu_5\text{-}\eta^2,P\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13} + 10H_2 \rightarrow$$
$$4Ru_4(\mu\text{-H})_3(\mu_4\text{-}\eta^2,P\text{-}HC_2PPh_2)(\mu\text{-}PPh_2)(CO)_{10} + Ru_4(\mu\text{-H})_4(CO)_{12}$$

Thus addition of H_2 to the open Ru_5 cluster has resulted in conversion of the acetylide to the parent alkyne and excission of one of the ruthenium carbonyl groups. The alkyne-bonded PPh_2 group again prevents aggregation of the open Ru_4 cluster, so that the relatively rare metallo-ligated triangular core is found. This reaction contrasts with those described earlier [10], where hydrogenation of, for example, $Ru_3(CO)_{10}$(dppm), resulted in cleavage of P—C bonds; in the present case, addition to the α-acetylenic carbon is preferred.

Experimental

A solution of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (100 mg, 0.079 mmol) in cyclohexane (40 cm^3) was hydrogenated in a 100 cm^3 autoclave (10 atm, 25° C, 18 h). The resulting burnt-yellow solution was taken to dryness and the residue chromatographed by preparative TLC [silica gel, light petroleum/ acetone (90/10)] to give seven bands. Band 1 (R_f 0.86) gave yellow $Ru_4(\mu\text{-}H)_4(CO)_{12}$ (9 mg, 16%) identified by its IR ν(CO) spectrum. Band 3 (R_f 0.48), yellow, was crystallised from CH_2Cl_2/MeOH to give yellow crystals of $Ru_4(\mu\text{-}H)_3(\mu_4\text{-}HC_2PPh_2)(\mu\text{-}PPh_2)(CO)_{10}$ (52 mg, 63%) m.p. 161–164°C. (Found: C, 39.98; H, 2.23; $C_{36}H_{24}O_{10}P_2Ru_4$ calcd.: C, 39.93; H, 2.23%). Infrared (cyclohexane): ν(CO) 2097m, 2071s, 2038vs, 2024s, 2012m, 1987m, 1977m cm^{-1}. ^1H NMR δ ($CDCl_3$) 9.10 (dd, J(PH) 2.6 and 18.1 Hz, 1H, C_2H), 7.24 (m, 20H, Ph), −15.40 (m, 1H, RuH), −18.53 (dm, J(PH) 24.0 Hz, 1H, RuH), −19.00 (dm, J(PH) 18.9 Hz, 1H, RuH). The remaining bands contained only trace amounts and were not identified.

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