Reactions of Tetranuclear Rhodium–Triruthenium Clusters with Di- and Tri-phosphines and with Alkynes†

Jean-Luc Le Grand, W. Edward Lindsell,* Kevin J. McCullough,* Calum H. McIntosh and A. Gavin Meiklejohn
Chemistry Department, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, UK

The compound $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(cp)]$ **1** (cp = $\eta^5\text{-}C_5H_5$) and an equimolar amount of diphosphine $Ph_2P(CH_2)_nPPh_2$ [n = 1 (dppm), 2 (dppe) or 3 (dppp)] react at ambient temperature principally with cleavage of the heteronuclear cluster to form several homonuclear rhodium and ruthenium products. Isolated ruthenium clusters are simple phosphine derivatives of $[Ru_3(CO)_{12}]$ or $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$, including $[Ru_3(\mu\text{-}diphos)_2(CO)_8]$ (diphos = dppm or dppe), $[Ru_3(\mu\text{-}diphos)(CO)_{10}]$ and $[\{Ru_3(\mu\text{-}diphos)(CO)_9\}_2(\mu\text{-}diphos)]$ (diphos = dppe or dppp), and $[Ru_4(\mu\text{-}H)_4(CO)_{10}(dppp)]$. Reaction of **1** with the triphosphine $MeC(CH_2PPh_2)_3$ affords hydrido-clusters $[Ru_3(\mu\text{-}H)H(\mu\text{-}triphos)(CO)_8]$ and $[Ru_3(\mu\text{-}H)\{\mu\text{-}PPhCH_2CMe(CH_2PPh_2)_2\}(CO)_8]$ **12**, the latter formed by elimination of benzene under very mild reaction conditions. The solid-state structure of cluster **12** has been determined by X-ray crystallographic analysis [monosolvate with dichloromethane, monoclinic, space group $P2_1/n$, a = 19.549(3), b = 14.2462(21), c = 16.429(4) Å, β = 90.271(18)°, Z = 4, R = 0.051, R' = 0.060] and the geometrical non-rigidity of this asymmetric molecule in solution is revealed by variable-temperature ^{31}P NMR spectroscopy. Reactions of cluster **1** with alkynes, RC≡CR (R = Ph or Et), give heteronuclear products, including isomers of $[RhRu_3(C_2R_2)(CO)_9(cp)]$ and trimetallic clusters $[RhRu_2(C_2R_2)(CO)_n(cp)]$ (R = Et, n = 7; R = Ph, n = 8); from reaction of $[RhRu_3(\mu\text{-}H)_4(CO)_9(\eta^5\text{-}C_5Me_5)]$ with PhC≡CPh a related tetranuclear cluster $[RhRu_3(C_2R_2)(CO)_9(\eta^5\text{-}C_5Me_5)]$ is formed. A new, octahedral heteronuclear cluster $[Rh_2Ru_4(\mu\text{-}H)_2(CO)_{12}(cp)_2]$ is also reported.

There is continuing interest in the chemistry[1] and the catalytic applications[2] of heteronuclear clusters. Following our previous investigations on the synthesis, geometrical non-rigidity and reactivity of tetranuclear ruthenium–rhodium clusters,[3–6] we report reactions of $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(cp)]$ **1** (cp = $\eta^5\text{-}C_5H_5$) with diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1–3) or the triphosphine $MeC(CH_2PPh_2)_3$, and with alkynes RC≡CR (R = Et or Ph), including the structural characterisation by X-ray diffraction of a product, $[Ru_3(\mu\text{-}H)\{\mu\text{-}PPhCH_2CMe(CH_2PPh_2)_2\}(CO)_8]$. A related reaction of $[RhRu_3(\mu\text{-}H)_4(CO)_9(\eta^5\text{-}C_5Me_5)]$ **2** with PhC≡CPh is described, and also a new hexanuclear cluster $[Rh_2Ru_4(\mu\text{-}H)_2(CO)_{12}(cp)_2]$. A preliminary account of the reactions between 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) and **1** has appeared.[7]

Results and Discussion

Reactions of Compound **1** *with Diphosphines* $Ph_2P(CH_2)_nPPh_2$ (n = 1–3).—At ambient temperature reaction of an equimolar mixture of bis(diphenylphosphino)methane (dppm) and cluster **1** in tetrahydrofuran (thf) affords the triruthenium compound $[Ru_3(\mu\text{-}dppm)_2(CO)_8]$ **3**[8] as the main product after chromatography, and no simple substitution products of the heteronuclear carbonyl cluster are isolable. A small amount of the yellow oxo-cluster $[Ru_3(\mu_3\text{-}O)(\mu_3\text{-}CO)(\mu\text{-}dppm)_2(CO)_5]$ **4**[9] can also be eluted from the column and this probably results from oxidation during the work-up of the reaction. Products from the reaction of 1,2-bis(diphenylphosphino)ethane (dppe) with **1** have been previously reported,[5] and with a 1:1 molar ratio of reactants the main product is $[Ru_3(\mu\text{-}dppe)_2(CO)_8]$ **5**.[10] Cluster **5** is the only isolable cluster from reactions containing dppe:**1** in ratios ⩾2:1. However, from reactions of 1,3-bis(diphenylphosphino)propane (dppp) with an equimolar amount of **1** the species $[Ru_3(\mu\text{-}dppp)_2(CO)_8]$ has not been identified and this may be a consequence of the unfavourable seven-membered rings of the two bridging bidentate ligands in this compound. The rhodium-containing species isolated from these reactions are principally $[Rh(CO)_2(cp)]$, $[Rh_2(\mu\text{-}CO)(CO)_2(cp)_2]$ and/or $[Rh_3(\mu\text{-}CO)_3(cp)_3]$.

Compounds **3** and **5** have related structures, the former having been previously characterised by X-ray diffraction in the solid state.[11] The five-membered Ru_2PCP ring systems of **3** give a well resolved AA′BB′ resonance in the $^{31}P\text{-}\{^1H\}$ NMR spectrum for the two pairs of inequivalent phosphorus atoms and show an essentially temperature-invariant 200 MHz ^1H NMR spectrum in the range −105 to +30 °C for the methylene (triplet resonance) and the aromatic hydrogen atoms. Therefore, although there is distortion to this bridging bidentate ligand ring in the solid state,[11] asymmetry due to this conformation is not detected by variable-temperature NMR spectroscopy; this may be due to facile ring inversion or to minimal difference in chemical shifts of the hydrogen atoms. On the other hand, the ^1H NMR spectrum of the hydrogen atoms associated with the six-membered Ru_2PC_2P rings of **5** is markedly temperature dependent: this is particularly noticeable for the methylene resonances which appear as a single broad complex band at ambient temperature (centre 2.0 ppm) but resolve into two broad bands at low temperature (δ 2.35 and 1.45, −90 °C). We attribute this observation to conformational inversion of the ring systems, previously observed in $[Os_3(\mu\text{-}dppe)(CO)_{10}]$,[12] in which equatorial and axial hydrogen atoms of the methylene groups are interchanged. Assuming that this inversion process involves two sites, a free energy of activation $\Delta G^{\ddagger}$ = 46 kJ mol^{-1} can be estimated[13] at the coalescence temperature of the resonances (−35 ± 3 °C). This inversion barrier is comparable with that observed for $[Os_3(\mu\text{-}dppe)(CO)_{10}]$.[12]

Reactions of dppe with compound **1** produced small quantities

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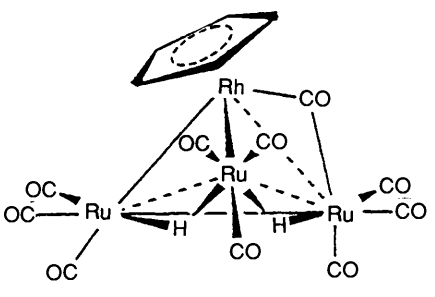
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



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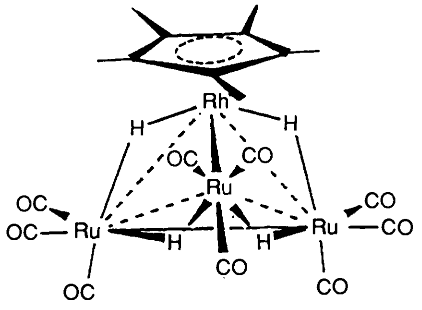

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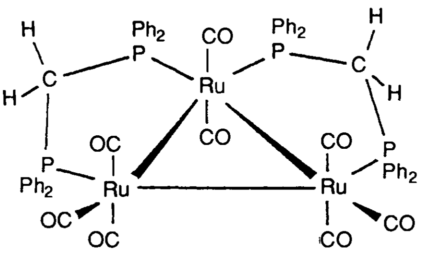

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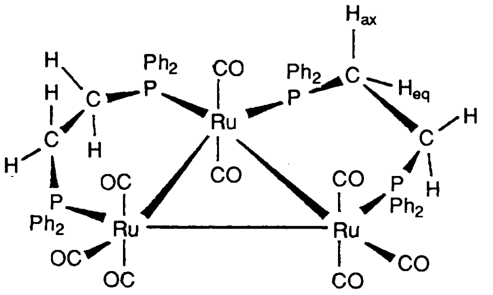

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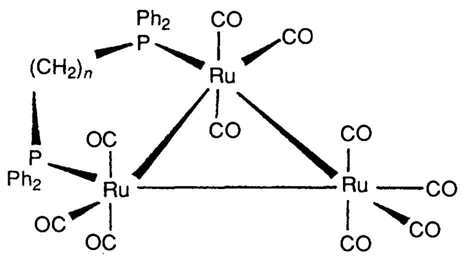
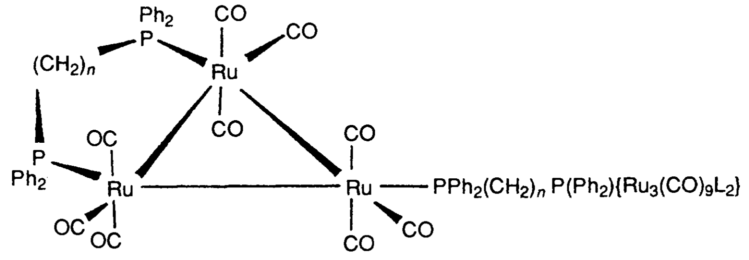
Table 1 Refined fractional atomic coordinates with estimated standard deviations for compound **12**

Atom	*x*	*y*	*y*	Atom	*x*	*y*	*z*
Ru(1)	0.777 04(6)	0.115 00(9)	0.543 11(7)	C(18)	0.791 4(4)	0.362 1(7)	0.771 3(6)
Ru(2)	0.665 77(7)	0.113 43(10)	0.427 58(8)	C(19)	0.797 5(4)	0.291 3(7)	0.713 1(6)
Ru(3)	0.765 22(6)	0.262 01(8)	0.420 90(7)	C(20)	0.885 3(4)	0.040 8(8)	0.695 6(7)
P(1)	0.866 37(20)	0.143 3(3)	0.633 64(24)	C(21)	0.860 2(6)	0.034 1(8)	0.774 8(7)
P(2)	0.843 84(20)	0.139 2(3)	0.427 09(23)	C(22)	0.869 8(6)	−0.048 3(8)	0.819 3(7)
P(3)	0.855 00(20)	0.365 6(3)	0.442 00(24)	C(23)	0.904 5(6)	−0.123 8(8)	0.784 8(7)
O(1)	0.786 1(8)	−0.096 1(9)	0.541 9(9)	C(24)	0.929 6(6)	−0.117 1(8)	0.705 6(7)
C(1)	0.783 0(8)	−0.017 6(13)	0.543 3(10)	C(25)	0.920 0(6)	−0.034 8(8)	0.661 1(7)
O(2)	0.676 6(7)	0.116 4(10)	0.683 3(8)	C(26)	0.862 6(5)	0.053 0(7)	0.347 3(5)
C(2)	0.712 5(8)	0.120 7(12)	0.629 1(10)	C(27)	0.876 1(5)	−0.039 9(7)	0.368 7(5)
O(3)	0.576 0(9)	−0.043 7(12)	0.494 2(10)	C(28)	0.893 9(5)	−0.104 9(7)	0.308 9(5)
C(3)	0.613 8(11)	0.009 2(13)	0.469 3(13)	C(29)	0.898 2(5)	−0.076 9(7)	0.227 7(5)
O(4)	0.724 6(7)	−0.021 8(13)	0.302 5(12)	C(30)	0.884 7(5)	0.016 0(7)	0.206 3(5)
C(4)	0.709 6(10)	0.030 5(14)	0.351 7(15)	C(31)	0.866 9(5)	0.081 0(7)	0.266 1(5)
O(5)	0.576 9(7)	0.183 1(10)	0.288 8(10)	C(32)	0.914 9(6)	0.397 3(8)	0.360 5(6)
C(5)	0.610 4(9)	0.157 4(13)	0.340 1(12)	C(33)	0.963 5(6)	0.467 1(8)	0.374 9(6)
O(6)	0.596 4(7)	0.241 3(11)	0.551 4(9)	C(34)	1.009 4(6)	0.492 1(8)	0.314 0(6)
C(6)	0.626 5(9)	0.196 5(13)	0.504 2(13)	C(35)	1.006 8(6)	0.447 3(8)	0.238 5(6)
O(7)	0.743 7(6)	0.267 4(9)	0.238 1(7)	C(36)	0.958 2(6)	0.377 5(8)	0.224 0(6)
C(7)	0.752 7(8)	0.267 7(11)	0.307 8(10)	C(37)	0.912 2(6)	0.352 5(8)	0.285 0(6)
O(8)	0.663 1(7)	0.416 1(9)	0.463 6(8)	C(38)	0.829 4(6)	0.481 1(7)	0.478 9(6)
C(8)	0.698 7(9)	0.356 2(13)	0.446 4(11)	C(39)	0.824 9(6)	0.501 5(7)	0.561 7(6)
C(9)	0.954 9(7)	0.233 9(11)	0.514 5(8)	C(40)	0.803 0(6)	0.590 0(7)	0.587 0(6)
C(10)	1.030 8(7)	0.261 0(12)	0.503 4(9)	C(41)	0.785 5(6)	0.658 0(7)	0.529 4(6)
C(11)	0.951 2(7)	0.174 0(11)	0.592 2(9)	C(42)	0.790 0(6)	0.637 6(7)	0.446 6(6)
C(12)	0.935 6(7)	0.173 4(10)	0.441 4(9)	C(43)	0.811 9(6)	0.549 1(7)	0.421 3(6)
C(13)	0.913 5(7)	0.328 5(10)	0.524 7(9)	Cl(1)	0.391 8(6)	0.276 7(8)	0.555 4(7)
C(14)	0.855 7(4)	0.234 7(7)	0.711 9(6)	Cl(2)	0.478 6(6)	0.385 4(8)	0.458 8(7)
C(15)	0.907 8(4)	0.248 9(7)	0.769 0(6)	C(44)	0.402 1(15)	0.369 7(20)	0.488 4(18)
C(16)	0.901 7(4)	0.319 7(7)	0.827 1(6)	H(1)	0.783(8)	0.227(12)	0.530(10)
C(17)	0.843 4(4)	0.376 3(7)	0.828 3(6)				

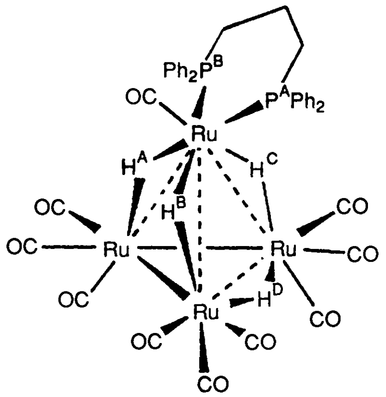
of a substitution product [$RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(\mu\text{-dppe})(CO)_7(cp)$],[5] but yields are low and we have been unable to isolate this cluster in significant amounts; cleavage of the $RhRu_3$ cluster is the dominant reaction pathway. Other than **5**, products which have been separated by chromatography after reactions with dppe are [$Ru_3(\mu\text{-dppe})(CO)_{10}$] **6**,[10] [$Rh_3(\mu\text{-}CO)_3(cp)_3$],[14] and a non-crystalline product of probable formula [$\{Ru_3(CO)_9(dppe)\}_2(\mu\text{-dppe})$] **7**. It may be noted that the compound



6 $n = 2$
8 $n = 3$



	n	L_2
7	2	dppe
10	3	dppp
11	3	$(CO)_2$



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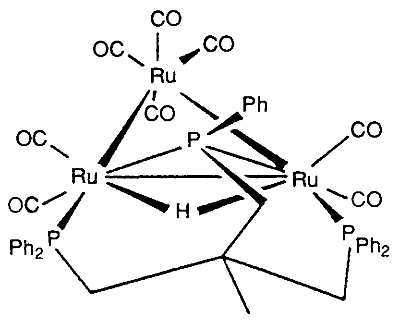

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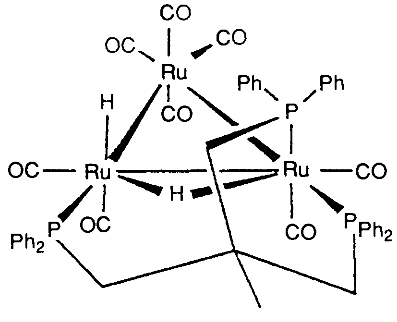

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$[\{Ru_3(CO)_9\}_2(diop)_3]$ [diop = 3,4-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane], of similar stoichiometry to **7**, has been reported[15] but isomeric structures are possible. Ions of the parent molecule are not present in the fast atom bombardment (FAB) mass spectrum of **7**, but fragmentation ions are observed.

Identified products, isolable after chromatography from reactions of dppp with **1**, are, in order of elution, $[Ru_3(\mu\text{-dppp})(CO)_{10}]$ **8**[16] $[Ru_4(\mu\text{-H})_4(CO)_{10}(dppp)]$ **9**, $[\{Ru_3(CO)_9(dppp)\}_2(\mu\text{-dppp})]$ **10** and, probably, $[\{Ru_3(CO)_9(dppp)\}\{Ru_3(CO)_{11}\}(\mu\text{-dppp})]$ **11**. Comparable IR spectra of **6** and **8** indicate that the dppp ligand is bridging in **8**, and μ-dppp

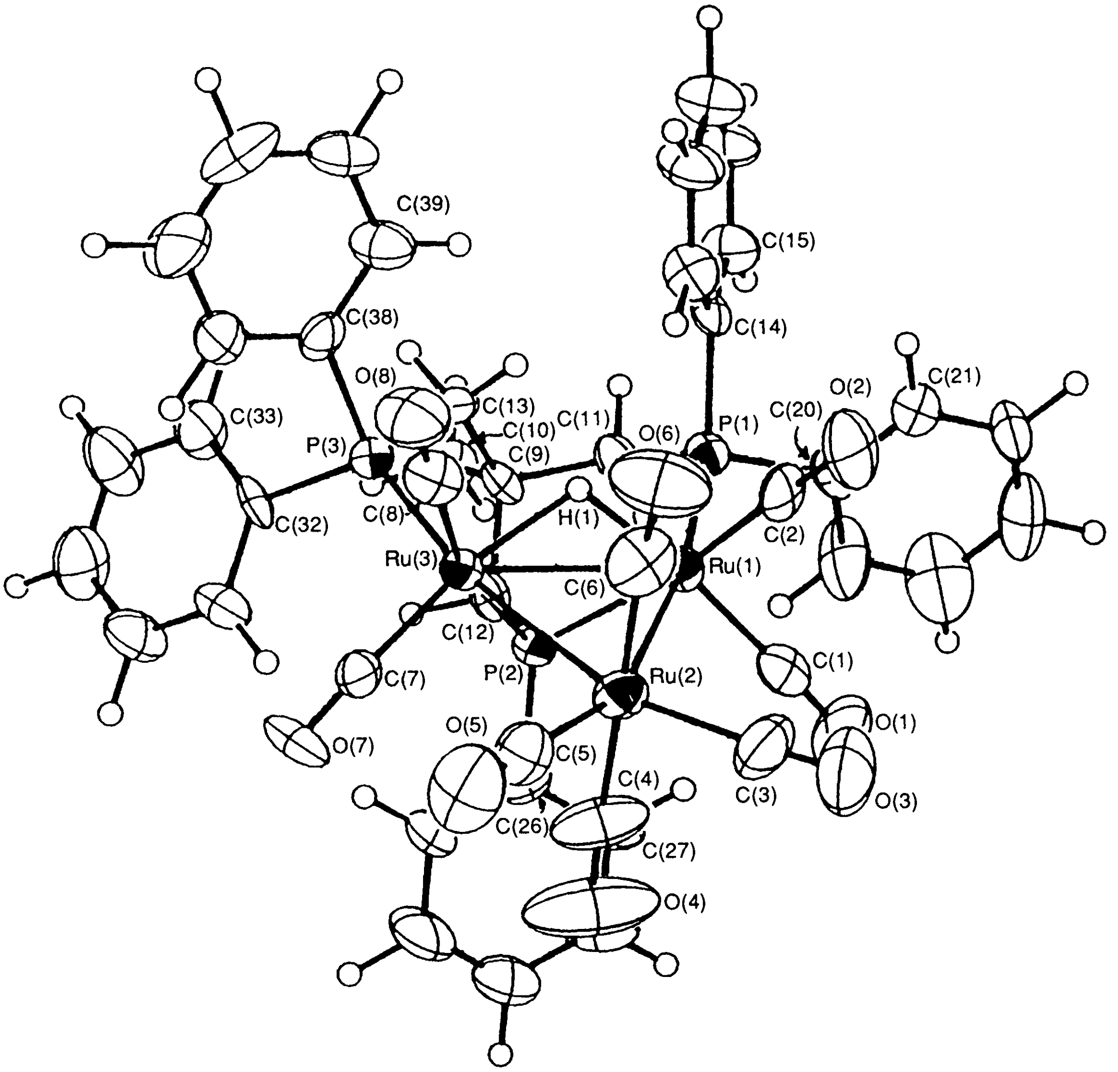


Fig. 1 The molecular structure of cluster **12** (ORTEP, 50% probability ellipsoids). Labels for the hydrogen atoms and some of the carbon atoms of the phenyl rings have been omitted for clarity

ligands are probably also present in the Ru_3 units of **10** and **11**. Phosphinated Ru_4 products are not isolated from the related reactions of dppm or dppe with **1**, even though $[Ru_4(\mu\text{-}H)_4(CO)_{10}(diphos)]$ (diphos = dppm[17] and dppe[18]) are known, so that the formation of **9** from dppp must be related to the nature of the ligand and the 'bite' of its longer chelating chain. Two isomers of $[Ru_4(\mu\text{-}H)_4(CO)_{10}(dppe)]$, containing either bridging or chelating dppe, have been reported[18] but it is clear from the spectral data that **9** has a structure related to that of the latter isomer with a $Ru_4(\mu\text{-}H)_4$ core of C_s symmetry and a chelated dppp forming, in this case, a six-membered ring. Cluster **9** shows similar fluxional behaviour to that of its dppe analogue[18] and this has been monitored by variable-temperature ^1H and ^{31}P NMR spectroscopy: at −55 °C a rigid system is observed with four non-equivalent metal-bonded hydrogens and two inequivalent phosphorus atoms, whereas three of the hydrogen atoms (H^A, H^B and H^D) undergo rapid interchange at ambient temperature and a single, broadened, phosphorus resonance results.

Reaction of Compound **1** *with* $(Ph_2PCH_2)_3CMe$ (*triphos*).—As with diphosphines, reaction of an equimolar amount of 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) with cluster **1** at room temperature causes cleavage of the heteronuclear skeleton to form ruthenium and rhodium fragments. After chromatography of the reaction mixture, rhodium is recovered mainly as $[Rh(CO)_2(cp)]$, and the triruthenium products $[Ru_3(\mu\text{-}H)\{\mu\text{-}PPhCH_2CMe(CH_2PPh_2)_2\}(CO)_8]$ **12** and $[Ru_3(\mu\text{-}H)H(\mu\text{-}triphos)(CO)_8]$ **13** are separated. Other ruthenium-containing hydrido-clusters, including small amounts of substituted $RhRu_3$ derivatives, are also produced but these could not be isolated in pure form and remain incompletely characterised. If the reaction is carried out at sub-ambient temperatures (0–10 °C) the yield of **13** is increased relative to that of cluster **12**.

The crystal and molecular structure of compound **12** was determined by X-ray analysis of its monosolvate with dichloromethane, obtained as monoclinic, orange-red prisms from light petroleum–dichloromethane. The structure is depicted in Fig. 1 with the relevant atom labelling. Tables 1 and 2 list the atomic fractional coordinates and selected, derived geometrical parameters, respectively. Cluster **12** contains a triangle of three ruthenium atoms with two unbridged Ru–Ru bonds [Ru(1)–Ru(2) 2.8803(18), Ru(2)–Ru(3) 2.8765(18) Å] and a slightly longer bond [Ru(1)–Ru(3) 2.9097(17) Å] bridged by one hydrogen atom, H(1), and a phosphide function, P(2), formed by dephenylation of a PPh_2 group of the triphosphine. The other two PPh_2 groups of the ligand are bonded as normal phosphorus(III) two-electron donors, one to each ruthenium atom, Ru(1) and Ru(3), to form a secondary bridging system and a heterocyclic cage of $Ru_2P_3C_4$ atoms. The terminal Ru–P bonds [2.324(4) and 2.318(4) Å] are shorter than the Ru–P bonds to the bridging phosphide atom [2.341(4) and 2.330(4)

Table 2 Selected derived geometrical parameters (distances in Å, angles in °) for complex **12**

Ru(1)–Ru(2)	2.8803(18)	Ru(2)–C(5)	1.902(19)	P(2)–C(12)	1.873(15)	O(6)–C(6)	1.165(25)
Ru(1)–Ru(3)	2.9097(17)	Ru(2)–C(6)	1.893(19)	P(2)–C(26)	1.835(11)	O(7)–C(7)	1.158(20)
Ru(1)–P(1)	2.324(4)	Ru(3)–P(2)	2.330(4)	P(3)–C(13)	1.848(14)	O(8)–C(8)	1.137(22)
Ru(1)–P(2)	2.341(4)	Ru(3)–P(3)	2.318(4)	P(3)–C(32)	1.839(12)	C(9)–C(10)	1.546(20)
Ru(1)–H(1)	1.61(17)	Ru(3)–H(1)	1.90(17)	P(3)–C(38)	1.825(11)	C(9)–C(11)	1.539(20)
Ru(1)–C(1)	1.892(16)	Ru(3)–C(7)	1.875(16)	O(1)–C(1)	1.121(22)	C(9)–C(12)	1.523(20)
Ru(1)–C(2)	1.900(16)	Ru(3)–C(8)	1.917(18)	O(2)–C(2)	1.139(21)	C(9)–C(13)	1.582(20)
Ru(2)–Ru(3)	2.8765(18)	P(1)–C(11)	1.847(15)	O(3)–C(3)	1.13(3)	Cl(1)–C(44)	1.73(3)
Ru(2)–C(3)	1.927(21)	P(1)–C(14)	1.842(10)	O(4)–C(4)	1.14(3)	Cl(2)–C(44)	1.59(3)
Ru(2)–C(4)	1.922(21)	P(1)–C(20)	1.817(12)	O(5)–C(5)	1.125(24)		

Ru(2)–Ru(1)–Ru(3)	59.58(4)	Ru(1)–Ru(2)–C(5)	157.1(6)	Ru(1)–P(1)–C(14)	118.8(3)	Ru(1)–Ru(3)–P(2)	51.64(10)
Ru(2)–Ru(1)–P(1)	170.42(11)	Ru(1)–Ru(2)–C(6)	82.2(6)	Ru(1)–P(1)–C(20)	111.7(4)	Ru(1)–Ru(3)–P(3)	107.30(11)
Ru(2)–Ru(1)–P(2)	83.52(10)	Ru(3)–Ru(2)–C(3)	159.7(6)	C(11)–P(1)–C(14)	101.2(6)	Ru(1)–Ru(3)–H(1)	30.9(51)
Ru(2)–Ru(1)–H(1)	88.8(60)	Ru(3)–Ru(2)–C(4)	97.1(6)	C(11)–P(1)–C(20)	102.5(6)	Ru(1)–Ru(3)–C(7)	136.4(5)
Ru(2)–Ru(1)–C(1)	92.3(5)	Ru(3)–Ru(2)–C(5)	96.4(6)	C(14)–P(1)–C(20)	101.5(5)	Ru(1)–Ru(3)–C(8)	113.9(5)
Ru(2)–Ru(1)–C(2)	89.3(5)	Ru(3)–Ru(2)–C(6)	80.9(6)	Ru(1)–P(2)–Ru(3)	77.05(12)	Ru(2)–Ru(3)–P(2)	83.79(10)
Ru(3)–Ru(1)–P(1)	111.94(11)	C(3)–Ru(2)–C(4)	89.7(9)	Ru(1)–P(2)–C(12)	118.3(5)	Ru(2)–Ru(3)–P(3)	166.96(11)
Ru(3)–Ru(1)–P(2)	51.31(10)	C(3)–Ru(2)–C(5)	102.9(8)	Ru(1)–P(2)–C(26)	126.7(4)	Ru(2)–Ru(3)–H(1)	83.7(51)
Ru(3)–Ru(1)–H(1)	37.3(60)	C(3)–Ru(2)–C(6)	91.7(9)	Ru(3)–P(2)–C(12)	116.2(5)	P(1)–C(11)–C(9)	118.9(10)
Ru(3)–Ru(1)–C(1)	136.4(5)	C(4)–Ru(2)–C(5)	88.1(8)	Ru(3)–P(2)–C(26)	127.2(4)	P(3)–C(13)–C(9)	118.7(10)
Ru(3)–Ru(1)–C(2)	115.6(5)	C(4)–Ru(2)–C(6)	177.4(9)	C(12)–P(2)–C(26)	94.0(6)	P(3)–C(38)–C(43)	117.9(8)
P(1)–Ru(1)–P(2)	94.31(14)	Ru(2)–Ru(3)–C(7)	89.1(5)	Ru(3)–P(3)–C(13)	113.2(5)	Ru(2)–C(5)–O(5)	179.1(17)
P(1)–Ru(1)–H(1)	81.6(60)	Ru(2)–Ru(3)–C(8)	92.7(5)	Ru(3)–P(3)–C(32)	122.1(4)	Ru(2)–C(6)–O(6)	172.7(17)
P(1)–Ru(1)–C(1)	97.2(5)	P(2)–Ru(3)–P(3)	88.42(14)	Ru(3)–P(3)–C(38)	114.5(4)	Ru(3)–C(7)–O(7)	177.1(14)
P(1)–Ru(1)–C(2)	91.0(5)	P(2)–Ru(3)–H(1)	68.9(51)	C(13)–P(3)–C(32)	102.3(6)	Ru(3)–C(8)–O(8)	174.9(16)
P(2)–Ru(1)–H(1)	72.9(60)	P(2)–Ru(3)–C(7)	99.1(5)	C(13)–P(3)–C(38)	100.6(6)	C(10)–C(9)–C(11)	106.6(11)
P(2)–Ru(1)–C(1)	96.5(5)	P(2)–Ru(3)–C(8)	164.6(5)	C(32)–P(3)–C(38)	101.3(5)	C(10)–C(9)–C(12)	106.4(11)
P(2)–Ru(1)–C(2)	166.9(5)	P(3)–Ru(3)–H(1)	83.7(51)	Ru(1)–H(1)–Ru(3)	111.8(92)	C(10)–C(9)–C(13)	107.0(11)
H(1)–Ru(1)–C(1)	169.2(61)	P(3)–Ru(3)–C(7)	102.5(5)	Ru(1)–C(1)–O(1)	178.7(15)	C(11)–C(9)–C(12)	109.2(11)
H(1)–Ru(1)–C(2)	96.0(61)	P(3)–Ru(3)–C(8)	92.1(5)	Ru(1)–C(2)–O(2)	173.5(15)	C(11)–C(9)–C(13)	111.0(11)
C(1)–Ru(1)–C(2)	94.7(7)	H(1)–Ru(3)–C(7)	166.6(51)	Ru(2)–C(3)–O(3)	170.6(19)	C(12)–C(9)–C(13)	116.2(11)
Ru(1)–Ru(2)–Ru(3)	60.72(4)	H(1)–Ru(3)–C(8)	95.8(51)	Ru(2)–C(4)–O(4)	168.4(19)	P(2)–C(12)–C(9)	118.6(10)
Ru(1)–Ru(2)–C(3)	99.7(6)	C(7)–Ru(3)–C(8)	95.8(7)	C(5)–C(2)–C(6)	93.8(8)	P(3)–C(38)–C(39)	122.1(8)
Ru(1)–Ru(2)–C(4)	95.4(6)	Ru(1)–P(1)–C(11)	118.6(5)	Ru(1)–Ru(3)–Ru(2)	59.70(4)		

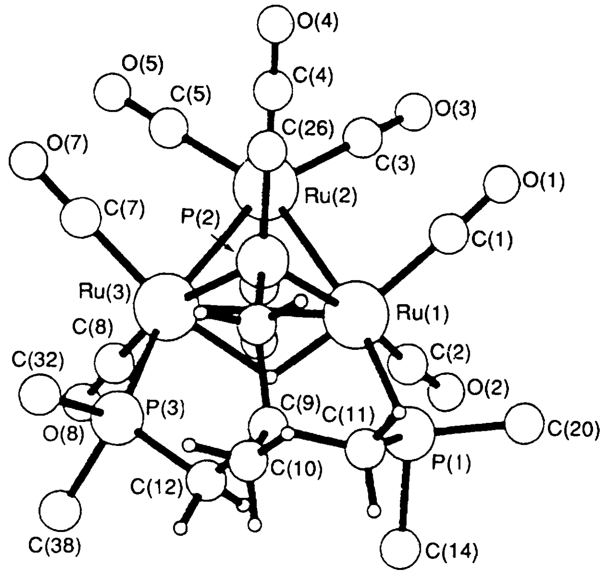
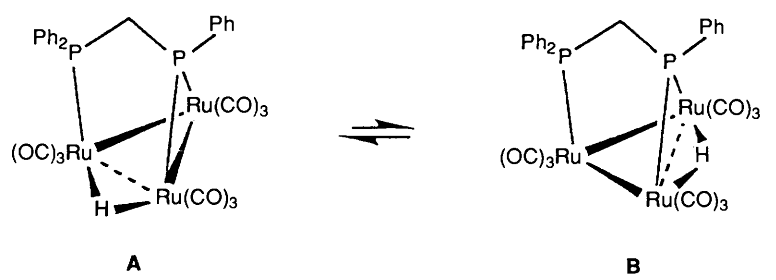


Fig. 2 The molecular structure of compound **12** (PLUTO) in the region of the $Ru_2P_3C_4$ cage system

Å]. The basic $Ru_3(\mu\text{-}H)(\mu\text{-}X)$ core is a well established structure for triruthenium clusters and in $[Ru_3(\mu\text{-}H)(\mu\text{-}PPhH)(CO)_{10}]$[19] the bridged Ru–Ru distance [2.903(1) Å] and the bridging Ru–P bonds (2.338 and 2.339 Å) are of comparable lengths to those reported here. As illustrated by Fig. 2, the conformation of the $Ru_2P_3C_4$ cage causes the cluster to be asymmetric. Phosphide atom P(2) lies 1.742 Å from the Ru_3 plane and the phosphine atoms P(1) and P(3), in formally equatorial ligand sites, are very slightly displaced to the opposite side of this plane (0.187 and 0.045 Å, respectively). The methylene groups and the pairs of phenyl substituents attached to P(1) and P(3) are, respectively, in differing molecular environments so that P(1) and P(3) are distinctly inequivalent in this solid-state structure, as is evident from Fig. 2.

Various μ-phosphido ruthenium clusters[17,20–23] have previously been formed in thermolytic reactions of diphosphorus ligands on Ru_3 or Ru_4 clusters. These reactions involve P–C and/or C–H bond cleavage at temperatures ⩾80 °C and some of the products incorporate the structural unit $Ru_2(\mu\text{-}H)(\mu\text{-}PRR')$. Formation of compound **12** involves dephenylation of triphos *via* P–C bond fission and elimination of a molecule of benzene. The cleavage of P–C bonds of ligands is a well documented reaction[24] but usually only occurs at elevated temperatures, whereas **12** is produced under the mild conditions of ⩽22 °C. It is of interest that hydrogenation at 80 °C of $[Ru_3(\mu\text{-}dppm)(CO)_{10}]$ or related species[20] forms $[Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]$ which has been structurally characterised in the solid state as **A**, with μ-hydrido and μ-phosphido bridges linking different pairs of Ru atoms. In solution, NMR spectra show that **A** is in equilibrium with a more symmetrical isomer **B**, assigned a structure with a bridging system more closely related to that of **12**.[20a]

The $^{31}P\text{-}\{^1H\}$ and ^1H NMR spectra of compound **12** in solution at ambient temperature are assignable to a molecule of apparent C_s symmetry, containing equivalent PPh_2 groups, but the cluster is fluxional. Variable-temperature $^{31}P\text{-}\{^1H\}$ NMR studies between +25 and −114 °C show that the single, doublet resonance of the two PPh_2 groups observed at higher temperatures transforms, at −114 °C, into two doublets of equal intensity, assignable to inequivalent atoms P(1) and P(3); this process occurs with a simple coalescence at −99 °C without the appearance of other resonances which could indicate the presence of alternative isomeric forms. Moreover, only one ^1H



NMR resonance is observed for the metal-bonded hydrogen, H(1), over the same temperature range; the symmetrical doublet of triplets at ambient temperature does become a broadened multiplet at the lowest temperatures, as atoms P(1) and P(3) become inequivalent on the NMR time-scale, but there is no evidence for the presence of a structurally different isomer as found for $[Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]$.[20a] Assuming that the single structure of **12** in solution is that of Fig. 1, the fluxionality must be attributed to interchange between enantiomeric forms of the asymmetric heterocyclic $Ru_2P_3C_4$ cage of the diruthenium–ligand system. Atoms P(1) and P(3) are inequivalent in the rigid structure but inversion of this cage can occur, involving, in particular, motion of the methylene groups and of the phenyl substituents attached to P(1) and P(3) (Scheme 1). A free energy of activation $\Delta G^{\ddagger}$ = 33 kJ mol^{-1} can be estimated for this inversion at the coalescence temperature of the $^{31}P\text{-}\{^1H\}$ NMR resonances.

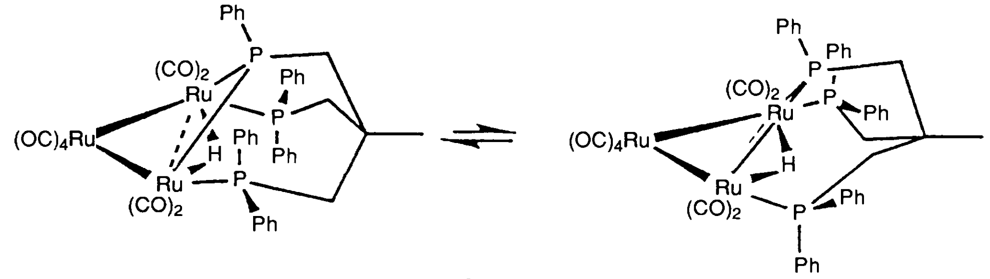
The structure of product **13** can be assigned on the basis of ^1H and ^{31}P NMR studies, including selective ^{31}P decoupling. The basic geometry is related to that of species $[Os_3(\mu\text{-}H)H(CO)_9L]$,[25] containing one terminal and one dibridging hydride ligand. The ligand triphos acts in a tridentate manner bridging the same two Ru atoms as μ-H, with two *cis* P atoms bonded to one ruthenium and a third *cis* to the terminal H atom on the other ruthenium. Variable-temperature ^1H NMR spectra of **13** over the range +30 to −100 °C show no evidence for geometrical non-rigidity. Cluster **13** slowly decomposes in solution at or above ambient temperature to form **12** as the major product after elimination of benzene. This process can be easily monitored by NMR spectroscopy, and in $CDCl_3$ at 24 °C the half-life of **13** is *ca.* 11 h.

The facile extrusion of benzene from compound **13** must be related to the proximity of a hydrogen ligand and a phenyl group in the cluster. Prior intramolecular oxidative addition of PPh to ruthenium, followed by reductive elimination of PhH, could be occurring but in this electronically saturated system a concerted loss of PhH seems a more probable mechanism. The *axial* PPh_2 group of the co-ordinated triphos possesses a very favourable geometry with respect to the terminal hydrogen ligand on the adjacent Ru atom to undergo intramolecular elimination of benzene with the formation of the bridging phosphide function in the product **12**. It may be noted that an interaction betwen a PPh unit and the adjacent, non-bridged Ru atom has been observed in the unsaturated cluster $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9]$.[26] Proton NMR studies of the decomposition of **13** at 24 °C, however, show that the process involves more than a unique one-step elimination. Although **12** is formed as the main product throughout the process, other hydrido-species are also observed and it is not clear whether these originate from separate decomposition pathways or are intermediates of the major pathway. Thus, in $CDCl_3$, new species with multiplet hydride resonances at δ −16.0 and −18.4 are also generated, but these disappear over 70 h leaving **12** as the only hydrido-cluster. In CD_2Cl_2–$CD_3C_6D_5$, a hydrido-product (δ −17.85) forms alongside **12** and is still present after 120 h at 24 °C.

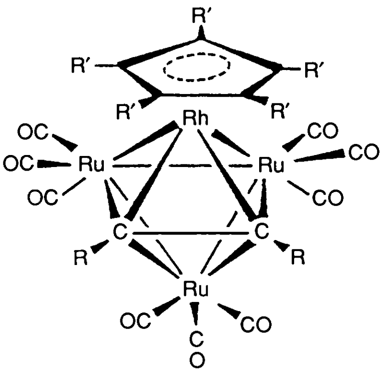
The formation of **12** in the original reaction of triphos with cluster **1** must arise, at least in part, *via* **13** and subsequent elimination of benzene. It should be noted, however, that even from reactions at 0–10 °C, when the yield of product **13** increases, significant amounts of **12** are still isolated and it is possible that alternative elimination mechanisms may also operate.

Reactions of Compound **1** *or* **2** *with Alkynes* RC≡CR (R = Ph *or* Et).—Cluster **1** reacts with diphenylacetylene or hex-3-yne at ambient temperature over 2–4 d to give a mixture of several cluster products, some of which can be separated by chromatography on a silica gel column. The reaction with an equimolar amount of diphenylacetylene affords at least six products after chromatography, including three clusters **15**–**17**, obtained in crystalline forms, and another, **14**, which is converted into **16** on attempted purification. Other minor products were not investigated. Four cluster products, **18**–**21**, can be isolated after chromatography using light petroleum, from reaction of **1** with a slight excess of hex-3-yne. However, product **19** could not be completely separated from small amounts of **18**, and all products **18**–**21** are initially contaminated with hydrocarbon residues which are probably derived from hex-3-yne, and include hydrogenated and oligomerised species. These hydrocarbon impurities are difficult to remove from small amounts of the hydrocarbon-soluble clusters.

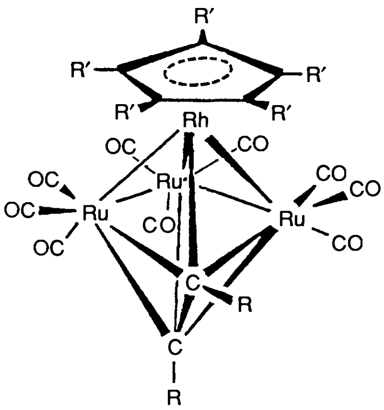
On the basis of spectroscopic studies (^1H and $^{13}C\text{-}\{^1H\}$ NMR, FAB mass and IR) cluster **16**, $[RhRu_3(C_2Ph_2)(CO)_9(cp)]$, can be assigned the structure illustrated containing a $RhRu_3C_2$ core with a 'butterfly' arrangement of metal atoms and a $\mu_4\text{-}\eta^2$-alkyne ligand. The Rh atom occupies a 'wing-tip' position, *cis* to both C atoms of the alkyne causing both PhC units to be equivalent in NMR spectra. A similar structure is assignable to **21**, $[RhRu_3(C_2Et_2)(CO)_9(cp)]$, obtained as a solid with associated hydrocarbon; this product has an IR spectrum resembling that of **16** and the FAB mass spectrum shows



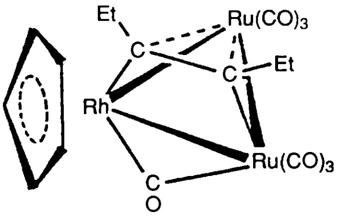
Scheme 1



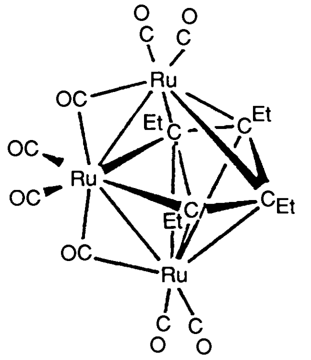
	R	R′
16	Ph	H
21	Et	H
22	Ph	Me



18 R = Et, R′ = H
(**14**? R = Ph, R′ = H)



19



20

molecular ions and the expected fragmentation pattern. The ^{1}H NMR spectrum of **21** is also consistent with this structure; in particular the methylene hydrogens of the two equivalent ethyl groups are individually inequivalent giving ABX$_3$ systems for ethyl groups bonded to asymmetric C atoms of the RhRu$_3$C$_2$ core. Product **18**, obtained as analytically pure crystals, is an isomer of **21**, with a very similar FAB mass spectrum but with a different IR spectrum, although still containing only terminal ν(CO) bands. The ^{1}H NMR spectrum of **18** differs from that of **21** and the resonances of the ethyl groups can be assigned to two slightly inequivalent, simple A$_2$X$_3$ systems attached to differing, non-chiral core C atoms. The proposed structure of **18**, [RhRu$_3$(C$_2$Et$_2$)(CO)$_9$(cp)] (illustrated), is isomeric with **21** containing the Rh atom at the 'hinge' position, *cis* to one core C atom and *trans* to the other, and with both C atoms lying in the plane of the overall C_s molecular symmetry. When heated for 15 h at 50–60 °C solutions of **18** partially decompose with the formation of some **21**, so that isomerisation between **18** and **21** does occur. Although product **14** from the reaction of diphenylacetylene was not isolated in a pure form, its IR spectrum showed some similarity to that of **18** and it was largely converted into **16** on attempted chromatographic purification, so that it may be tentatively proposed that **14** is the isomer of **16** with the Rh atom at the 'hinge' position.

Reaction of diphenylacetylene with [RhRu$_3$(μ-H)$_4$(CO)$_9$(η^5-C$_5$Me$_5$)] **2** is slow at ambient temperature, but on warming an equimolar mixture of these reagents in thf at 50 °C for 2 h transformation into [RhRu$_3$(C$_2$Ph$_2$)(CO)$_9$(η^5-C$_5$Me$_5$)] **22** occurs. Product **22**, which is the only new cluster isolable after chromatography, has analytical data, FAB mass, IR and ^{1}H NMR spectra supporting a *closo*-RhRu$_3$C$_2$ stystem with a structure analogous to that of the cyclopentadienyl derivative **16**.

The *closo*-M$_4$C$_2$ arrangement of skeletal atoms is well established in carbonyl cluster chemistry[27] and heteronuclear triruthenium species structurally related to **16**, **18**, **21** and **22** (and possibly **14**) include [FeRu$_3$(C$_2$Ph$_2$)(CO)$_{12}$],[28] [CoRu$_3$(C$_2$Ph$_2$)(μ-CO)$_2$(CO)$_9$]$^-$,[29] and [MRu$_3$(C$_2$Me$_2$)(μ-CO)$_2$(CO)$_8$(cp)]$^-$ (M = Mo or W).[30] Also, the rhodium-containing cluster [Co$_2$Rh$_2$(C$_2$Ph$_2$)(CO)$_{10}$][31] may be noted. Two isomers of the types discussed above have been characterised for [FeRu$_3$(C$_2$Ph$_2$)(CO)$_{12}$] and thermal isomerisation between them has been reported.[28] The isomer with Fe at a 'wing-tip' site is thermodynamically more stable, present in 9 : 1 ratio in an equilibrium mixture with the other form at 70 °C, and this corresponds with our observations for the new RhRu$_3$C$_2$ species, *i.e.* the isolation of **16** or **22** as major products from reactions with PhC≡CPh, and the conversion of **18** into **21**. In these reactions alkyne appears to prefer insertion into a Rh–Ru bond. However, in the formation of [FeRu$_3$(C$_2$Ph$_2$)(CO)$_{12}$] by reaction of [FeRu$_3$(μ-H)$_2$(CO)$_{13}$] with diphenylacetylene in boiling hexane the less thermodynamically stable isomer, containing Fe in a 'hinge' position, is reported to be formed initially as the kinetic product,[28] so that any speculation on the mechanism of reaction of cluster **1** with alkynes may not be justified. It may also be noted that only the isomer with Co at a 'wing-tip' has been reported[29] for [CoRu$_3$(C$_2$Ph$_2$)(μ-CO)$_2$(CO)$_9$]$^-$, whereas only the other form, with the heteroatom at a 'hinge' site, is found for clusters [MRu$_3$(C$_2$RR′)(μ-CO)$_2$(CO)$_8$(cp)]$^-$ (M = Mo or W; R = R′ = Me; R = Ph, R′ = H).[30]

Two further cluster products **19** and **20** are isolable from the reaction of **1** with hex-3-yne. Compound **20** has been identified by spectroscopic studies as the known cluster[32] $[Ru_3(C_4Et_4)(\mu\text{-}CO)_2(CO)_6]$, reportedly isostructural with the black isomer of $[Fe_3(C_2Ph_2)_2(CO)_8]$,[32b] and containing two linked alkynes forming a five-membered metallocyclic ring with one Ru atom and bonding to the other two Ru atoms to give a formal pentagonal-bipyramidal *closo*-Ru_3C_4 core. Cluster **19** could not be isolated in an analytically pure form, being contaminated with a little **18** and some hydrocarbon residues, but FAB mass, ^1H NMR and IR studies support its formulation as $[RhRu_2(C_2Et_2)(CO)_7(cp)]$, with ethyl groups attached to inequivalent, asymmetric C atoms and with a bridging carbonyl group. The structure illustrated is consistent with the data. It contains a four-electron μ_3-$\eta^2(\|)$-alkyne in a *nido*-$RhRu_2C_2$ arrangement of core atoms with Ru in the axial site and this geometry is well known[27,33] in species such as $[Os_3(C_2Ph_2)(CO)_{10}]$, $[Ru_3H_2(C_2Ph_2)(CO)_9]$, $[Co_2Fe(C_2R_2)(CO)_9]$, $[FeNi_2(C_2R_2)(CO)_3(cp)_2]$ and $[CoFeNi(C_2R_2)(CO)_6(cp)]$ with the same polyhedral electron count (p.e.c.) as that of **19**.

Two other cluster products **15** and **17** are also isolated from reactions of **1** with diphenylacetylene but these are not structural analogues of products from the reaction with hex-3-yne. Although the known orange-yellow species[34] $[Ru_3(C_4Ph_4)(\mu\text{-}CO)_2(CO)_6]$, structurally related to **20**, was separated as a minor contaminant during purification of partially decomposed samples of **15**, the major product, **15**, contains the uncleaved $RhRu_3$ core and at least two alkyne units; a possible formula is $[RhRu_3(C_2Ph_2)_2(CO)_n(cp)]$ but this characterisation is uncertain. The red crystalline product **17** is a cluster of $RhRu_2$ but the IR spectrum does not resemble that of **19** and contains no bands assignable to bridging carbonyl ligands. Analytical, ^1H NMR and FAB mass spectral data support the formulation $[RhRu_2(C_2Ph_2)(CO)_n(cp)]$, with n = 8, since this is clearly the composition of the well defined, highest peak in the mass spectrum. With this formula and a triangular $[(cp)Rh]Ru_2$ system, the alkyne is probably acting as a simple two-electron donor giving a p.e.c. of 48 electrons.

Attempts to characterise several of the above alkyne-derived clusters structurally by X-ray diffraction were unsuccessful since suitable crystals could not be obtained.

Formation of the Hexanuclear Cluster $[Rh_2Ru_4(\mu\text{-}H)_2(CO)_{12}(cp)_2]$ **23**.—By-products can be isolated from preparations of cluster **1** using $[Ru_3(CO)_{12}]$, $[Rh(CO)_2(cp)]$ and H_2 as reagents, if the reactions are carried out at higher temperatures than usual, *i.e.* > 100 °C, and particularly if $[Rh(CO)_2(cp)]$ is contaminated with some $[Rh_2(\mu\text{-}CO)(CO)_2(cp)_2]$. NMR investigations of these by-products indicate that, initially, a mixture of species is isolated after chromatography: two main hydride-containing clusters, accompanied by two or three minor species. Careful purification of the mixture by chromatography and crystallisation only yielded one pure crystalline product, **23**. On the basis of analysis, FAB mass, NMR and IR spectroscopic studies **23** is $[Rh_2Ru_4(\mu\text{-}H)_2(CO)_{12}(cp)]$, containing a bridging carbonyl with a single IR band at 1803 cm^{-1}. The two hydride ligands are equivalent at ambient temperature in the ^1H NMR spectrum, appearing as a triplet resonance with a small coupling to ^{103}Rh (7.9 Hz). The p.e.c. of 86 is consistent with an octahedral Rh_2Ru_4 system but the location of μ-H and μ-CO ligands is not certain. Unfortunately the crystals of **23** obtained did not give satisfactory diffraction for X-ray analysis.

Conclusions

Reactions of $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(cp)]$ **1** with di- and tri-phosphines in equimolar quantities at mild ambient temperatures lead primarily to cleavage of the heterometallic core to yield $(cp)Rh(CO)_n$ fragments, isolated variously as $[Rh(CO)_2(cp)]$, $[Rh_2(\mu\text{-}CO)(CO)_2(cp)_2]$ and/or $[Rh_3(\mu\text{-}CO)_3(cp)_3]$, and a range of phosphinated ruthenium clusters. Phosphine derivatives of Ru_3 or linked-Ru_3 clusters are prominent products; in particular $[Ru_3(\mu\text{-}diphos)_2(CO)_8]$ from dppm or dppe, and $[\{Ru_3(CO)_9(\mu\text{-}diphos)\}_2(\mu\text{-}diphos)]$ from dppe or dppp, are formed with elimination of hydrogen from **1**. From the longer diphosphine dppp significant amounts of the tetranuclear tetrahydrido-cluster $[Ru_4(\mu\text{-}H)_4(CO)_{10}(dppp)]$, containing the chelating, non-bridging ligand, are also formed. The triphosphine $MeC(CH_2PPh_2)_3$, on the other hand, gives ruthenium clusters retaining hydrogen ligands, including $[Ru_3(\mu\text{-}H)H(\mu\text{-}triphos)(CO)_8]$ which readily transforms into $[Ru_3(\mu\text{-}H)\{\mu\text{-}PPhCH_2CMe(CH_2PPh_2)_2\}(CO)_8]$ by elimination of benzene. Reactions of alkynes with **1**, under mild conditions, or with $[RhRu_3(\mu\text{-}H)_4(CO)_9(\eta^5\text{-}C_5Me_5)]$ **2**, at slightly higher temperatures (50 °C), give clusters $[RhRu_3(C_2R_2)(CO)_9(cp)]$ containing *closo*-$RhRu_3C_2$ cores as main products, with the major isomer having Rh at a 'wing-tip' position of the $RhRu_3$ 'butterfly' and being formally derived from the precursor by insertion of alkyne into a Rh–Ru bond. Cleavage into homonuclear fragments is not so dominant for reactions of **1** with alkynes as with di- or tri-phosphines but $[Rh(CO)_2(cp)]$ and $[Ru_3(CO)_{12}]$ are important by-products, and alkyne derivatives of the heterotrimetallic $RhRu_2$ core are formed as well as small amounts of derivatives $[Ru_3(C_4R_4)(\mu\text{-}CO)_2(CO)_6]$.

Experimental

All reactions were carried out using Schlenk techniques under an atmosphere of dry, gaseous nitrogen using freshly distilled, predried solvents, as previously described.[3,5] Starting clusters $[RhRu_3(\mu\text{-}H)_2(\mu\text{-}CO)(CO)_9(cp)]$ **1** and $[RhRu_3(\mu\text{-}H)_4(CO)_9(\eta^5\text{-}C_5Me_5)]$ **2** were prepared as reported.[3] The following reagents were obtained commercially and used as supplied: $Ph_2P(CH_2)_nPPh_2$ (n = 1, dppm; n = 2, dppe; n = 3, dppp), and $MeC(CH_2PPh_2)_3$ (triphos) (Strem Chemicals); hex-3-yne (BDH); diphenylacetylene (Aldrich). Silica gel used for column chromatography was 70–230 mesh (Merck) and the light petroleum had a boiling range of 60–80 °C, unless otherwise specified. The NMR spectra were recorded at *ca.* 25 °C, unless otherwise stated, on a Bruker WP 200 SY spectrometer at 200 and 50.3 MHz, respectively, for ^1H and ^{13}C, using $SiMe_4$ as reference, and at 81.0 MHz for ^{31}P, with 85% H_3PO_4 as reference: chemical shifts, δ (ppm), to high frequencies are quoted as positive. In some cases, to assist in assignments of parameters of complex resonances, ^1H NMR spectra were also recorded at 80.1 MHz on a Bruker WP 80 SY spectrometer. Infrared spectra were obtained on a Perkin-Elmer 1600 FT or 580 spectrometer, and FAB mass spectra on a Kratos MS 50 TC instrument, at the University of Edinburgh, using matrices of the clusters in *m*-nitrobenzyl alcohol. Elemental analyses were determined at University of Manchester Institute of Science and Technology and/or at the University of Edinburgh.

Reactions of Cluster **1**.—*With bis(diphenylphosphino)methane.* Cluster **1** (100 mg, 0.132 mmol) and dppm (52 mg, 0.135 mmol) were stirred in thf (10 cm^3) at room temperature for 18 h. Chromatography with light petroleum eluted $[Rh(CO)_2(cp)]$ and unreacted **1**.

Light petroleum–dichloromethane (1:1) eluted $[Ru_3(\mu\text{-}dppm)_2(CO)_8]$ **3**, obtained as red crystals (20 mg) after recrystallisation (Found: C, 54.1; H, 3.8. $C_{58}H_{44}O_8P_4Ru_3$ requires C, 53.7; H, 3.4%). IR (cyclohexane) ν(CO): 2044w, 1992w, 1973(sh), 1968vs and 1945w cm^{-1} [lit.:[8] 2056w, 2046w, 2023m, 2012(sh), 1998(sh), 1981vs, 1970s and 1945m cm^{-1}]. NMR ($CDCl_3$): ^1H, δ 7.0–7.4 (complex, C_6H_5, 20 H) and 4.06 [t, J(PH) 9.8, CH_2, 2 H]; ^{31}P-$\{^1H\}$, centre δ 20.8 {AA′BB′ multiplet, parameters from computer simulation (PANIC), δ_A 21.8, δ_B 18.7 [J(AA′) 25.2, J(AB) 54.5, J(BB′) 2.8, J(AB′) ≈ 0.1 Hz]}.

Dichloromethane–acetone (1:1) eluted a yellow band which afforded yellow crystals (2 mg) of $[Ru_3(\mu_3\text{-}O)(\mu_3\text{-}CO)(\mu\text{-}dppm)_2(CO)_5]$ **4**. IR(cyclohexane) ν(CO): 2023vs, 1992m, 1961vs, 1944w, 1933w and 1688w cm^{-1} (lit.:[9] 2021, 1992, 1961, 1943, 1933 and 1689 cm^{-1}). NMR: ^{1}H (CDCl$_3$), δ 6.7–7.7 (complex m, C_6H_5) and 3.0–3.6 (br m, CH_2); ^{31}P-{^{1}H} [$(CD_3)_2CO$)], centre δ 29.3 (AA′BB′ m, $\delta_A \approx 29.7$, $\delta_B \approx 29.0$). FAB mass spectrum: M^+ (*m*/*z* 1258, ^{102}Ru$_3$) and $[M - n\text{CO}]^+$ (n = 1–4, n = 3 dominant).

Finally, methanol eluted a small brown band of an uncharacterised product, leaving some material on the column.

With 1,2-bis(diphenylphosphino)ethane. Reactions of cluster **1** with an equimolar quantity of dppe in thf were carried out as reported.[5] As before the main product isolated after chromatography was invariably [Ru$_3$(μ-dppe)$_2$(CO)$_8$] **5**, although the yield of the previously reported by-product eluted by dichloromethane–acetone (1:1) and assigned a structure [RhRu$_3$(μ-H)$_2$(μ-CO)(CO)$_7$(dppe)(cp)] was very low or negligible. Other by-products were also isolated after chromatography as follows.

Light petroleum–dichloromethane (1:1) eluted a small amount of orange [Ru$_3$(μ-dppe)(CO)$_{10}$] **6**. IR (light petroleum) ν(CO): 2083m, 2017s, 2000s, 1981vw, 1968w and 1937w cm^{-1} [lit. (hexane):[10] 2080, 2014, 1999, 1981, 1965 and 1935 cm^{-1}]. NMR (CDCl$_3$): ^{1}H, δ 7.43 (m, C_6H_5, 20 H) and 2.30/2.11 (A_2B_2, CH_2CH_2, 4 H); ^{31}P-{^{1}H}, δ 40.7 (s). FAB mass spectrum: M^+ (*m*/*z* 984, ^{102}Ru$_3$) and $[M - n\text{CO}]^+$ (n = 1–10).

Acetone–dichloromethane (1:4) eluted at least three products, including green C_{3v} [Rh$_3$(μ-CO)$_3$(cp)$_3$] [IR (CH$_2$Cl$_2$): 1850s and 1795s cm^{-1} (lit.:[14] 1849 and 1793, cm^{-1}). ^{1}H NMR (CD$_2$Cl$_2$): δ 5.52 (s, C_5H_5)] and a yellow-brown product of probable formula [{Ru$_3$(CO)$_9$(dppe)}$_2$(μ-dppe)] **7** (Found: C, 49.0; H, 3.6. $C_{96}H_{72}O_{18}P_6Ru_6$ requires C, 50.0; H, 3.1%. IR (CH$_2$Cl$_2$) ν(CO): 2042w, 1988s and 1966(sh) cm^{-1}. NMR (CD$_2$Cl$_2$): ^{1}H δ 7.5 (br s, C_6H_5), 2.15 and 2.52 (complex, CH_2); ^{31}P-{^{1}H}, δ 38.7 (br) and 31.0 (br). FAB mass spectrum: band of ions of highest *m*/*z* centred at 1575 {possibly [Ru$_6$(CO)$_6$(dppe)$_2$]$^+$, 1576, ^{102}Ru$_6$}; other prominent bands at 1461, 1406, 1346).

With 1,3-bis(diphenylphosphino)propane. Cluster **1** (100 mg, 0.13 mmol) and dppp (58 mg, 0.14 mmol) were stirred in thf (10 cm^3) for 18 h at ambient temperature. Chromatography of the reaction mixture gave the following products. Light petroleum eluted [Rh(CO)$_2$(cp)]; light petroleum–CH$_2$Cl$_2$ (9:1) eluted some unreacted **1**.

Light petroleum–CH$_2$Cl$_2$ (8:1) eluted a small yellow band to give [Ru$_3$(μ-dppp)(CO)$_{10}$] **8** (*ca.* 3 mg). IR (light petroleum) ν(CO): 2084m, 2017vs, 2002s, 1981w, 1966w and 1920w cm^{-1} [lit. (hexane):[16] 2078, 2011, 2001, 1964 and 1919 cm^{-1}]. ^{1}H NMR (CDCl$_3$): δ 7.42, 7.47 (complex, C_6H_5, 20 H), 2.55 (m, CH_2, 4 H) and 1.7 (m, CH_2, 2 H). FAB mass spectrum: M^+ (*m*/*z* 998, ^{102}Ru$_3$), $[M - n\text{CO}]^+$ (n = 1 – 10, n = 4 dominant), and Ru$_2$ fragment ions.

Light petroleum–CH$_2$Cl$_2$ (4:1) eluted a yellow-orange band which yielded [Ru$_4$(μ-H)$_4$(CO)$_{10}$(dppp)] **9** as orange needles (5 mg) after crystallisation from light petroleum–CH$_2$Cl$_2$ at −15 °C (Found: C, 39.7; H, 2.7. $C_{37}H_{30}O_{10}P_2Ru_4$ requires C, 40.4; H, 2.7%). IR (CH$_2$Cl$_2$) ν(CO): 2080s, 2045s, 2024s, 2000s and 1982(sh) cm^{-1}. NMR (CDCl$_3$): ^{1}H, δ 7.2–7.5 (complex, C_6H_5, 20 H), 2.65 and 2.45 (complex, CH_2, 4 H), 1.67 (complex, CH_2, 2 H), 16.42 (br, μ-H, 3 H) and −17.84 [tq, *J*(PH) 8, *J*(HH) 2.8, μ-H, 1 H] (fluxional, see text); (−55 °C), hydride resonances (assignments by selective ^{31}P decoupling), δ −15.51 [dd, *J*(P^{A}H) 30.3, *J*(P^{B}H) 14.6, H^A], −16.64 (s, H^D), −17.12 [dd, *J*(P^{A}H) 18.5, *J*(P^{B}H), 27.7, H^B] and −17.96 [br t, *J*(PH) 8, H^C]; ^{31}P-{^{1}H}, δ 21.2 (br $\Delta\nu_{\frac{1}{2}}$ 120 Hz) (fluxional, see text); (−25 °C), δ 27.3 [d, *J*(PP) 35 Hz, P^B] and 14.6 (d, P^A).

Light petroleum–CH$_2$Cl$_2$ (2:1) initially eluted a small orange band which gave an uncharacterised product and, secondly, an orange-red band which yielded red, prismatic crystals (8 mg) of [{Ru$_3$(CO)$_9$(dppp)}$_2$(μ-dppp)] **10**, on crystallisation from the mixed solvent at −15 °C (Found: C, 51.4; H, 3.7. $C_{99}H_{78}O_{18}P_6Ru_6$ requires C, 50.6; H, 3.3%). IR (CH$_2$Cl$_2$) ν(CO): 2050m, 1981vs (br) and 1966(sh) cm^{-1}. NMR (CDCl$_3$): ^{1}H, δ 7.1–7.6 (complex, C_6H_5), 2.58 and 2.25 (br, CH_2) and 0.8–1.5 (complex, CH_2); ^{31}P-{^{1}H}, δ 26.5 [d, *J*(PP) 14 Hz, 2 P], 20.8 and 20.7 [d and s (overlapping), 4 P]. FAB mass spectrum: band of ions of highest *m*/*z* centred at 1520 {probably [Ru$_6$(CO)$_3$(dppp)$_2$]$^+$, 1520, ^{102}Ru$_6$}; other prominent bands centred at 1492 and 1388.

Light petroleum–CH$_2$Cl$_2$ (1:1) eluted a blue-green band which gave a green solid (*ca.* 3 mg). IR (CH$_2$Cl$_2$) ν(CO): 2063s, 2024s, 2008s and 1993(sh) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.0–7.7 (complex, C_6H_5) and 5.2 (s, C_5H_5). FAB mass spectrum: band of ions of highest *m*/*z* centred at 1399; other prominent bands centred at 1313, 1286, 1258, 1231, 1204, 1171, 1145 and 720.

Acetone–CH$_2$Cl$_2$ eluted several yellow-orange bands. One orange band gave an orange-brown solid (9 mg) product, probably [Ru$_6$(CO)$_{20}$(dppp)$_2$] **11** (Found: C, 44.7; H, 3.8. $C_{74}H_{52}O_{20}P_4Ru_6$ requires C, 44.6; H, 2.6%). IR (CH$_2$Cl$_2$) ν(CO): 2042m and 1960vs(br) cm^{-1}. NMR (CDCl$_3$): ^{1}H, δ 7.42 (br, C_6H_5), 2.6, 2.45, 2.2, 1.7 and 1.5 (br, CH_2); ^{31}P-{^{1}H}, δ 32.5 [d, *J*(PP) 3, 1 P], 27.4 [dd, *J*(PP) 13.7 and 3 Hz, 1 P], and 20.8 (br, probably overlapping s and d, 2 P).

Methanol eluted a further uncharacterised orange band, leaving some material on the column.

With 1,1,1-tris(diphenylphosphinomethyl)ethane. Cluster **1** (100 mg, 0.13 mmol) and triphos (80 mg, 0.13 mmol) were stirred in thf (10 cm^3) for 18 h at ambient temperature. The reaction mixture was evaporated to dryness under vacuum and the residue chromatographed on a column of silia gel. Light petroleum eluted a little [Rh(CO)$_2$(cp)] and then some unreacted **1** (*ca.* 7 mg).

Light petroleum–CH$_2$Cl$_2$ (5:2) eluted a yellow-orange band which afforded orange prisms (15 mg) of **12**, as a solvate with dichloromethane, [Ru$_3$(μ-H){μ-PPhCH$_2$CMe(CH$_2$PPh$_2$)$_2$}-(CO)$_8$]·CH$_2$Cl$_2$, after crystallisation from light petroleum–CH$_2$Cl$_2$ at −15 °C (Found: C, 45.1; H, 3.3. $C_{44}H_{37}Cl_2O_8P_3Ru_3$ requires C, 45.5; H, 3.2%). IR (light petroleum) ν(CO): 2071m, 2010s, 2004(sh), 1990m and 1952w, cm^{-1}. NMR: ^{1}H (CDCl$_3$), δ 7.4, 7.7 and 8.1 (complex, C_6H_5, 25 H), 5.29 (s, CH_2Cl_2, 2 H), 2.1 (complex, CH_2, 4 H), 1.52 (d, CH_2, 2 H), 0.52 (s, CH_3, 3 H) and −17.06 [dt, *J*(P^{C}H) 25.2, *J*(P$^{A/B}$H) 8.6, μ-H, 1 H]; ^{31}P-{^{1}H} (CDCl$_3$), δ 107.6 [t, *J*(PP) 27, PPh, 1 P] and 24.6 (d, PPh$_2$, 2 P); (CD$_2$Cl$_2$–CFCl$_3$, −114 °C), δ 108.4 (≈t, PPh, 1 P), 26.7 [d, *J*(PμP) 22, PPh$_2$, 1 P] and 23.9 [d, *J*(PμP) 30 Hz, PPh$_2$, 1 P].

Light petroleum–CH$_2$Cl$_2$ (1:1) eluted an orange band giving a red-brown solid (5 mg), comprising a mixture of two (or more) hydrido-clusters. ^{1}H NMR (CDCl$_3$): metal–hydrogen resonances, δ −16.4, −16.6 and −18.5 (complex, relative intensity 2:1:1, respectively).

Dichloromethane eluted a yellow-orange band which gave deep red–microcrystals (5 mg) of [Ru$_3$(μ-H)H(μ-triphos)-(CO)$_8$] **13** on crystallisation from light petroleum–CH$_2$Cl$_2$ at −15 °C [a better yield (*ca.* 15 mg) of **13**, but less **12**, was obtained when the reaction was conducted at 0–10 °C, and the chromatography carried out within 2 h at ambient temperature] (Found: C, 51.1; H, 3.8. $C_{49}H_{41}O_8P_3Ru_3$ requires C, 51.0; H, 3.8%). IR (CH$_2$Cl$_2$) ν(CO): 2038s, 2005vs, 1985vs, 1945m and 1918w cm^{-1}. NMR (CDCl$_3$, −25 °C): ^{1}H, δ 6.4–7.9 (complex, C_6H_5, 30 H), 3.35, 2.7 and 1.8 (complex, CH_2, 6 H), 1.1 (s, CH_3, 3 H), −11.61 [m, *J*(HH) 3, *J*(P^{A}H) 5, RuH, 1 H] and −17.14 [dt, *J*(P^{C}H) 10, *J*(P$^{A/B}$H) 20, RuHRu, 1 H); ^{31}P-{^{1}H}, δ 34.2 [dd, *J*(P^{A}P) 3.8, *J*(P^{B}P) 30.8, P^C], 22.4 (dd, P^A), and 15.4 [dd, *J*(P^{A}P) 2.7 Hz, P^B].

Acetone–CH$_2$Cl$_2$ (1:1) eluted a small band, giving an uncharacterised, dark brown solid [^{1}H NMR (CDCl$_3$): metal–hydrogen resonance, δ −16.5], leaving some material on the column.

With diphenylacetylene. To cluster **1** (98 mg, 0.13 mmol) in thf (50 cm^3) was added a slight molar excess of PhC≡CPh (25 mg, 0.14 mmol) and the solution was stirred for 42 h at ambient temperature. The thf was removed by evaporation under vacuum and the residue was chromatographed on a column of silica gel. Light petroleum eluted some [Ru$_3$(CO)$_{12}$] and [Rh(CO)$_2$(cp)] followed by a brown band (14 mg) containing product **14**, contaminated with some unreacted starting material **1**. Attempted purification by rechromatography resulted in conversion into cluster **16** (see below), so that pure **14** could not be isolated. Spectroscopic features: IR (light petroleum) ν(CO): 2070w, 2052s, 2028s, 2000s, 1984w, and 1961vw cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.0–7.8 (complex, C_6H_5) and 5.25 [d, *J*(RhH) 0.6 Hz, C_5H_5].

Light petroleum–dichloromethane (20:1) eluted a red band giving incompletely characterised compound **15**, as microcrystals (22 mg). IR (light petroleum) ν(CO): 2081w, 2075w, 2052m, 2040m, 2028s, 2005w, 1994w, 1975w and 1965vw cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.8–6.8 (complex, C_6H_5, 20 H) and 5.43 [d, *J*(Rh–H) 0.69 Hz, C_5H_5, 5 H]. FAB mass spectrum: cluster ion bands centred at *m*/*z* 1116w, 1086w, 1060s, 1030w, 1005s, 976w, 958vw, 948w, 930s, 920vs, 903w, 893m, 872w, 864vw, 844vw, 836m, 818m and 807vs.

Light petroleum–dichloromethane (10:1) eluted a purple band which yielded small, purple prisms of compound **16** on crystallisation at −15 °C (28 mg) (Found: C, 37.0; H, 1.7. $C_{28}H_{15}O_9RhRu_3$ requires C, 37.3; H, 1.7%). IR (light petroleum) ν(CO): 2074s, 2036s, 2025s, 2007m, 1999w, 1988vw, 1976m, 1969(sh) and 1960vw cm^{-1}. NMR: ^{1}H ($CDCl_3$), δ 7.02 (s, C_6H_5, 10 H) and 5.29 [d, *J*(RhH) 0.63, C_5H_5, 5 H]; ^{13}C-{^{1}H} (CD_2Cl_2), δ 200.5 (br, CO), 183.3 [d, *J*(RhC) 17.7, Ph*C*≡*C*Ph], 158.1 (s, *ipso*-C_6H_5), 131.3(s), 127.6(s) and 126.9(s) (*o*-, *m*- and *p*-C_6H_5), 90.8 [d, *J*(Rh–C) 5.9 Hz, C_5H_5]. FAB mass spectrum: M^+ (*m*/*z* 904, $^{102}Ru_3$) and $[M - n\text{CO}]^+$ (*n* = 3–9).

Light petroleum–dichloromethane (10:1) subsequently eluted a small yellow band, which was not investigated, and dichloromethane eluted a red fraction giving thin, red needles (4 mg) of compound **17**, as an adduct with CH_2Cl_2, on recrystallisation from light petroleum–dichloromethane at −15 °C (Found: C, 38.9; H, 1.5. $C_{27}H_{15}O_8RhRu_2{\cdot}CH_2Cl_2$ requires C, 39.2; H, 2.0%). IR (light petroleum) ν(CO): 2077s, 2047vs, 2015s, 2005(sh) 1996m and 1981w cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.13–6.73 (two complex multiplets, C_6H_5, 10 H) and 5.66 [d, *J*(RhH) 0.84 Hz, C_5H_5, 5 H]. FAB mass spectrum: $[RhRu_2(PhC_2Ph)(CO)_n(cp)]^+$ (*n* = 8–0, highest *m*/*z* = 774, $^{102}Ru_2$) and $[Ru_2(PhC_2Ph)(CO)_n]^+$ (*n* = 4–2, 0).

Finally, acetone removed a small orange band, leaving some material on the column.

With hex-3-yne. A solution containing cluster **1** (54 mg, 0.72 mmol) and hex-3-yne (8.8 mg, 0.11 mmol) in thf (10 cm^3) was stirred at room temperature for 4 d, during which time all cluster **1** had reacted (as shown by TLC). The solvent was removed under vacuum and the residue was chromatographed on a column of silica gel. Light petroleum sequentially eluted four bands which were collected (fourth band eluted by addition of CH_2Cl_2 to the light petroleum). A product was isolated from each band, as given below in order of elution, after evaporation of solvent to produce a concentrated solution and subsequent cooling to −15 °C.

(*i*) Purple-brown crystals (*ca*. 10 mg) of compound **18** (Found: C, 30.5; H, 1.7. $C_{20}H_{15}O_9RhRu_3$ requires C, 29.8; H, 1.9%). IR (light petroleum) ν(CO): 2067m, 2044s, 2022s, 1993vs and 1981s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.23 [d, *J*(RhH) 0.63, C_5H_5, 5 H], 3.10 [q, *J*(HH) 7.4, CH_2, 2 H], 3.08 [q, *J*(HH) 7.5, CH_2, 2 H] and 1.16 [t, *J*(HH) 7.5 Hz, CH_3, 6 H]. FAB mass spectrum: M^+ (*m*/*z* 808, $^{102}Ru_3$), $[M - n\text{CO}]^+$ (*n* = 1–9, with *n* = 2 dominant), and lower-intensity fragment-ion peaks containing a $RhRu_2$ core.

(*ii*) Red-brown, oily solid (*ca*. 5 mg) of slightly impure compound **19**. IR (light petroleum) ν(CO): 2067s, 2034s, 1998s, 1982w, 1973w and 1874vw (br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.51 [d, *J*(RhH) 0.7, C_5H_5, 5 H], 3.03 (m, A component of ABX_3 system, CH*H*, 1 H), 2.69 (m, B component of ABX_3 system, *C*HH, 1 H), 2.2 (complex m, CH_2, 2 H), 1.27 [t, *J*(HH) 7.4, CH_3, 3 H] and 1.15 [t, *J*(HH) 7.4 Hz, CH_3, 3 H]. FAB mass spectrum: M^+ {$[RhRu_2(C_2Et_2)(CO)_7(cp)]$, *m*/*z* 650, $^{102}Ru_2$}, $[M - n\text{CO}]^+$ (*n* = 1–7, with *n* = 2 dominant), and additional weaker peaks of higher *m*/*z*, assignable to ions of **18**, present as a minor impurity.

(*iii*) Yellow solid (*ca*. 5 mg) of $[Ru_3(C_4Et_4)(\mu\text{-}CO)_2(CO)_6]$ **20**. IR (light petroleum) ν(CO): 2062m, 2021s, 2002m, 1970s, 1878m and 1858m cm^{-1} [lit. (CCl_4):[32] 2064, 2021, 2003, 1972, 1879 and 1855 cm^{-1}]. FAB mass spectrum: M^+ (*m*/*z* 694, $^{102}Ru_3$), $[M - (n\text{CO} + m\text{H})]^+$ (*n* = 1–6) {also a lower intensity peak at *m*/*z* 856, possibly $[Ru_3(C_6H_{10})_4(CO)_8]^+$, 858, $^{102}Ru_3$}.

(*iv*) Brown-purple solid (*ca*. 10 mg) of compound **21**, contaminated with hydrocarbon residue (Found: C, 39.8; H, 4.1. $C_{20}H_{15}O_9RhRu_3{\cdot}2C_6H_{14}$ requires C, 39.3; H, 4.4%). IR (light petroleum) ν(CO): 2070s, 2030s, 2022s, 1992m, 1984(sh) and 1966m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.48 [d, *J*(RhH) 0.65, C_5H_5, 5 H], 2.87 (m, A component of ABX_3 system *C*HHCH$_3$, 2 H), 2.73 (m, B component of ABX_3 system CH*H*CH$_3$, 2 H), 1.06 [t, *J*(HH) 7.4 Hz, CH_2, 6 H]; also 0.81–0.89 and 1.24 (CH_3 and CH_2, respectively, of hydrocarbon, hexane or similar). FAB mass spectrum: M^+ (*m*/*z* 808, $^{102}Ru_3$) and $[M - n\text{CO}]^+$ (*n* = 1–9, with *n* = 2 dominant).

Reaction of Cluster **2** *with Diphenylacetylene*.—To cluster **2** (58 mg, 0.073 mmol) in thf (20 cm^3) was added PhC≡CPh (13 mg, 0.73 mmol) and the solution stirred. The reaction was heated to 50 °C for 2 h, and then allowed to cool to ambient temperature and left for 72 h. The thf was removed by evaporation under vacuum and the residue was chromatographed on a column of silica gel. Dichloromethane eluted an orange band (containing principally unreacted **2**) (10 mg), followed by a purple band which gave compound **22** as purple-brown crystals (21 mg) on crystallisation from light petroleum–dichloromethane (Found: C, 41.0; H, 2.5. $C_{33}H_{25}O_9RhRu_3$ requires C, 40.8; H, 2.6%). IR (light petroleum) ν(CO): 2070s, 2030s, 2017s, 2001w, 1995(sh), 1982vw and 1961m cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.06 (s, C_6H_5, 10 H) and 1.47 [s, $C_5(CH_3)_5$, 15 H]. FAB mass spectrum: M^+ (*m*/*z* 974, $^{102}Ru_3$) and $[M - n\text{CO}]^+$ (*n* = 1–9). A dark green band remained on the column and could not be eluted.

Formation of $[Rh_2Ru_4(\mu\text{-}H)_2(CO)_{12}(cp)_2]$ **23**.—In preparations of cluster **1** by passing hydrogen gas through a heated solution of $[Ru_3(CO)_{12}]$ (400 mg, 0.63 mmol) and excess of $[Rh(CO)_2(cp)]$ in octane[3] some previously unreported cluster by-products were isolated in low yields. The yield of $[Rh_2Ru_4(\mu\text{-}H)_2(CO)_{12}(cp)_2]$ **23**, and associated species, increases if the reaction is conducted at 110 °C (rather than at 90 °C as previously reported[3]), and if the reagent $[Rh(CO)_2(cp)]$ is contaminated with significant amounts of $[Rh_2(\mu\text{-}CO)(CO)_2(cp)_2]$. Chromatography on a column of silica gel, using light petroleum and light petroleum–CH_2Cl_2 (9:1) eluted unchanged reagents, $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$, and cluster **1** (*ca*. 40%).

Dichloromethane eluted a deep brown band containing a mixture of hydrido-cluster products in variable yields (10–30 mg). Proton NMR ($CDCl_3$) spectroscopy indicated the presence of two main constituents (and two or three minor products): (*i*) cluster **23** see below; (*ii*) δ 5.11 (s, C_5H_5, 15 H) and −15.91 [dt, *J*(RhH) 4.7 (d) and 13.5 (t) Hz, μ-H, 4 H], probably $[Rh_3Ru_3(\mu\text{-}H)_4(CO)_n(cp)_3]$ ($n \approx 8$).

Rechromatography of this mixture with light petroleum–CH_2Cl_2 (1:1) separated cluster **23**, obtained as dark brown crystals from light petroleum–CH_2Cl_2 at −15 °C (Found: C, 24.2; H, 1.2. $C_{22}H_{12}O_{12}Rh_2Ru_4$ requires C, 24.5; H, 1.1%). IR (light petroleum) ν(CO): 2070s, 2040vs, 2008s, 1999s, 1976m, 1968m and 1803m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.54 (s, C_5H_5, 10 H) and −17.14 [t, *J*(RhH) 7.9 Hz, μ-H, 2 H]. FAB mass spectrum: M^+ (*m*/*z* 1082, $^{102}Ru_4$), $[M - n\text{CO}]^+$ (*n* = 1–10), and fragment ions formed by loss of H and/or C_5H_5 {also, a weaker band around *m*/*z* = 1064, possibly $[Rh_3Ru_3H_2(CO)_9(C_5H_5)_3]^+$}. Other brown, decomposition species were partially eluted from the column with CH_2Cl_2 and with acetone, but the other hydrido-clusters in the original mixture were not isolable.

Crystal Structure Determination of $[Ru_3(\mu\text{-}H)\{\mu\text{-}PPhCH_2CMe(CH_2PPh_2)_2\}(CO)_8]{\cdot}CH_2Cl_2$ **12**.—A single crystal of compound **12** (from light petroleum–dichloromethane, approximate size 0.225 × 0.15 × 0.175 mm), mounted in a Lindemann tube, was used for X-ray data collection.

Crystal data. $C_{43}H_{35}O_8P_3Ru_3\cdot CH_2Cl_2$, $M = 1160.8$, orange-red prisms, monoclinic, space group $P2_1/n$ (non-standard setting of no. 14), $a = 19.549(3)$, $b = 14.2462(21)$, $c = 16.429(4)$ Å, $\beta = 90.271(18)°$, $U = 4575.3$ Å^3, $Z = 4$, $D_c = 1.685$ g cm^{-3}, $F(000) = 2304$, μ(Mo-Kα) = 12.30 cm^{-1}.

Data collection. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer over the quadrant (θ range 1.50–22.0°; h −20 to +20, k 0 to 15, l −17 to 0) using graphite-monochromated Mo-Kα X-radiation ($\lambda = 0.710\,693$ Å) and ω–2θ scanning. Of the 5592 unique data measured, 2762 had $I > 3\sigma(I)$ and were used in subsequent structural solution and refinement. The data were corrected for Lorentz and polarisation effects, and for absorption (DIFABS[35]).

Structure solution. The approximate locations of the Rh, Ru and P atoms were determined by direct methods (SHELXS 86[35]). After two cycles of refinement the remaining non-hydrogen atoms were located from a Fourier difference map phased on the refined heavy-atom positions. The structure was refined by block-matrix least-squares methods (SHELX 76[35]) using anisotropic thermal parameters for all the non-hydrogen atoms except for the Cl and C atoms of the dichloromethane molecule. All the hydrogen atoms were located on Fourier difference maps and included in the refinement process at idealised positions except for the bridging hydrogen atom H(1) whose positional parameters were allowed to refine as normal. The phenyl rings were treated as idealised hexagons (C–C 1.395, C–H 0.95 Å) with fixed isotropic thermal parameters for the hydrogen atoms ($U_{iso} = 0.10$ Å^2). At convergence, the discrepancy factors R and R' were 0.051 and 0.060 respectively. The weighting scheme, $w^{-1} = [\sigma^2(F) + 0.000\,64\,(F)^2]$, gave satisfactory analyses of variance. The final Fourier difference map was essentially featureless, general noise level less than ±0.32 e Å^{-3}, except for four peaks at *ca.* 0.77–0.87 e Å^{-3} of no apparent chemical significance in the region around the metal cluster. Incidental crystallographic calculations and compilation of tables were carried using the computer program CALC.[35] Figs. 1 and 2 were drawn using ORTEP[35] and PLUTO[35] respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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