Synthesis of Pentanuclear Clusters derived from $[Ru_3RhH_2(CO)_{10}(PPh_3)(\mu\text{-}COMe)]$. Crystal Structures of $[Ru_3Rh_2H_2(CO)_{12}(PPh_3)_2]$ and $[Ru_3RhAuH(CO)_{10}(PPh_3)_2(\mu_3\text{-}COMe)]$†

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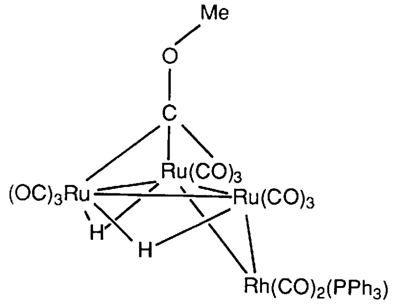
Reaction of $[Ru_3RhH_2(CO)_{10}(PPh_3)(\mu\text{-}COMe)]$ **2** with $K[BHBu^s_3]$ and then $[Rh(CO)_3(PPh_3)_2][PF_6]$ afforded $[Ru_3Rh_2H_2(CO)_{12}(PPh_3)_2]$ **3** in 29% yield. A single-crystal X-ray diffraction characterisation of compound **3** was carried out: monoclinic, space group *C*2/*c* (no. 15), $a = 19.409(4)$, $b = 9.944(6)$, $c = 26.153(4)$ Å, $\beta = 103.35(2)°$, $Z = 4$ and $R = 0.033$. A trigonal-bipyramidal cluster framework of C_2 symmetry was established, with an equatorial Ru_3 plane, and apical $Rh(CO)(PPh_3)$ units. The hydride ligands cap two triangular faces. Using $[Au(PPh_3)Cl]$ as an alternative electrophile, $[Ru_3RhAuH(CO)_{10}(PPh_3)_2(\mu_3\text{-}COMe)]$ **4** and $[Ru_3RhAuH_2(CO)_{11}(PPh_3)_2]$ **5** were formed in 5 and 19% yields, respectively. Complex **4** was characterised by X-ray diffraction: triclinic, space group $P\bar{1}$ (no. 2), $a = 11.361(3)$, $b = 13.745(4)$, $c = 17.124(3)$ Å, $\alpha = 74.15(2)$, $\beta = 74.59(2)$, $\gamma = 73.02(2)°$, $Z = 2$ and $R = 0.037$. This cluster also showed a trigonal-bipyramidal framework, with an equatorial Ru_2Rh plane and capping $AuPPh_3$ and $Ru(CO)_2$ units. There are three bridging ligands: the COMe ligand bridges the Ru_3 face, one CO bridges a Rh–Ru(apical) bond, and the hydride a Ru_2Rh face. Both these clusters are 72-electron species.

There has been considerable interest in possible synergistic effects between the metals in heteronuclear cluster complexes in terms of specific reactivity or enhancement of catalytic activity.[1] However, attempts to identify cluster-centred catalytic activity in particular have often been thwarted by dynamic cluster fragmentation, which often apparently generates highly reactive, co-ordinatively unsaturated species of lower nuclearity. Therefore approaches have been adopted to stabilise clusters against fragmentation, either by means of bridging bi- or tri-dentate ligands,[2] interstitial atoms,[3] or face-bridging ligands.[4] Having previously studied triruthenium–coinage metal clusters stabilised by a face-bridging methoxymethylidyne ligand,[5] we have attempted to synthesise mixed-metal clusters in which both elements might be the site of a range of organometallic reactions, namely ruthenium and rhodium. Thus the addition of a $[Rh(CO)_2(PPh_3)]^+$ unit to $[Ru_3H_2(CO)_9(\mu_3\text{-}COMe)]^-$ was carried out to form a Ru_3Rh tetranuclear cluster.[6] Subsequent reactions of this tetranuclear cluster $[Ru_3RhH_2(CO)_{11}(PPh_3)(\mu_3\text{-}COMe)]$ **1** resulted in the transformation of the face-bridging carbyne ligand, through an edge-bridging site in $[Ru_3RhH_2(CO)_{10}(PPh_3)(\mu\text{-}COMe)]$ **2** to a carbonyl group. In this report we extend the series of these heteronuclear clusters derived from $[Ru_3H_3(CO)_9(\mu_3\text{-}COMe)]$ to pentanuclear species, which also serve to illustrate two alternative modes in which the general synthetic strategy of electrophilic substitution at a cluster can proceed.



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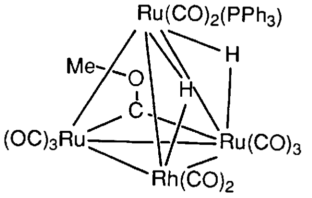

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Experimental

The general experimental procedures were as described in ref. 5, with the addition of fast atom bombardment mass spectrometry (FAB-MS) facilities now being employed on a VG7250-SE instrument using *m*-nitrobenzyl alcohol as the matrix. The following compounds were prepared by established methods: $[Au(PPh_3)Cl]$,[7] $[Rh(CO)_3(PPh_3)_2][PF_6]$[8] and $[Ru_3RhH_2(CO)_{10}(PPh_3)(\mu\text{-}COMe)]$ **2**.[6,9]

Preparation of $[Ru_3Rh_2H_2(CO)_{12}(PPh_3)_2]$ **3**.—A solution of $[Ru_3RhH_2(CO)_{10}(PPh_3)(\mu\text{-}COMe)]$ **2** (173 mg, 0.174 mmol) in tetrahydrofuran (thf) (30 cm^3) at room temperature was treated with 1.0 mol dm^{-3} $K[BHBu^s_3]$–thf (0.174 cm^3) and the resultant solution stirred for 15 min. The solution was then evaporated to dryness (vacuum line) and solid $[Rh(CO)_3(PPh_3)_2][PF_6]$ (164 mg, 0.191 mmol) added followed by CH_2Cl_2 (30 cm^3) at −90 °C. The solution was allowed to warm to room temperature (30 min), evaporated to dryness, and the solid residue chromatographed on a silica column. The required

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Summary of crystal data for $[Ru_3Rh_2H_2(CO)_{12}(PPh_3)_2]$ **3** and $[Ru_3RhAuH(CO)_{10}(PPh_3)_2(\mu_3\text{-}COMe)]$ **4**

	3	**4**
Formula	$C_{48}H_{32}O_{12}P_2Rh_2Ru_3$	$C_{48}H_{34}AuO_{11}P_2RhRu_3$
M	1371.58	1451.82
System	Monoclinic	Triclinic
Space group	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)
a/Å	19.409(4)	11.361(3)
b/Å	9.944(6)	13.745(4)
c/Å	26.153(4)	17.124(3)
α/°	90.0	74.15(2)
β/°	103.35(2)	74.59(2)
γ/°	90.0	73.02(2)
U/Å^3	4911.2	2409.4
Z	4	2
D_c/g cm^{-3}	1.855	2.001
D_m/g cm^{-3}	1.86(2)	2.00(2)
$F(000)$	2672	1392
μ(Mo-Kα)/cm^{-1}	16.24	43.52
Crystal size/mm	0.75 × 0.50 × 0.13	0.25 × 0.20 × 0.07
2θ range (min., max.)/°	3, 50	2, 50
ψ-Scan transmission (min., max.) (%)	61.2, 100.0	67.3, 100.0
Data recorded	4725	8959
Unique data recorded	4302	8485
Unique observed data [$F > 3\sigma(F)$]	3507	6369
No. of variables	307	419
R	0.033	0.037
R'	0.039	0.038

product was isolated as a black solid from the fifth band (dark orange) using light petroleum (b.p. 40–60 °C)–CH_2Cl_2 (2:1 v/v) as the eluent. Recrystallisation from CH_2Cl_2 and EtOH and washing with EtOH (3 × 10 cm^3 portions) finally gave compound **3** (69 mg, 29%) (Found: C, 42.3; H, 2.4. $C_{48}H_{32}O_{12}P_2Rh_2Ru_3$ requires C, 42.0; H, 2.4%). FAB-MS showed the M^+ and loss of nCO groups ($n = 3-8$). Compound **3** is moderately soluble in CH_2Cl_2 and thf, sparingly soluble in non-polar organic solvents, and insoluble in MeOH and EtOH.

IR: ν(CO)/cm^{-1} (in CH_2Cl_2) 2071m, 2042vs, 2021vs, 1999s, 1980s, 1968(sh), 1948m, 1824m and 1812m. NMR ($CDCl_3$): ^{1}H, δ 7.1–7.6 (m, Ph, 30 H) and −19.20 (m, μ-H, 2 H); ^{31}P, δ 15.5 [d, J(RhP) 132]; ^{13}C (at 223 K), δ 225.5 [d, J(RhC) 44, 1 C], 203.4 (s, 1 C), 199.5 (d, J 11, 1 C), 191.4 (s, 1 C), 190.4 [dd, J(RhC) 85, J(PC) 15 Hz, 1 C], 184.0 (s, 1 C) and 134–128 (Ph).

Preparation of $[Ru_3RhAuH(CO)_{10}(PPh_3)_2(\mu_3\text{-}COMe)]$ **4** *and* $[Ru_3RhAuH_2(CO)_{11}(PPh_3)_2]$ **5**.—A solution of compound **2** (208 mg, 0.209 mmol) in thf (30 cm^3) at room temperature was treated with 1.0 mol dm^{-3} $K[BHBu^s{}_3]$–thf (0.209 cm^3) and the resultant solution stirred for 15 min. The solution was then evaporated to dryness (vacuum line) and solid $[Au(PPh_3)Cl]$ (109 g, 0.219 mmol) added followed by CH_2Cl_2 (30 cm^3) at −90 °C. After allowing the solution to warm to room temperature (30 min) it was evaporated to dryness and the solid residue chromatographed on a silica column. Compounds **5** and **4** were isolated as red solids from the third and fourth bands (both red) respectively using light petroleum–CH_2Cl_2 (3:1 and 2:1 v/v respectively) as the eluents. This finally gave **5** (57 mg, 19%) and **4** (15 mg, 5%) [Found: C, 39.5; H, 2.5. $C_{48}H_{34}AuO_{11}P_2RhRu_3$ **4** requires C, 39.7; H, 2.4%; FAB-MS shows M^+ and fragment ions for CO loss (n = 1, 3–8). Found: C, 39.4; H, 2.3. $C_{47}H_{32}O_{11}AuP_2RhRu_3$ **5** requires C, 39.3; H, 2.2%]. The compounds are very soluble in CH_2Cl_2, and partially soluble in non-polar organic solvents.

Compound **4**. IR: ν(CO)/cm^{-1} (cyclohexane) 2060s, 2030vs, 2010vs, 1998m, 1983s, 1971s, 1960m, 1950m, 1940s, 1865m and 1857w. NMR ($CDCl_3$): ^{1}H, δ 7.0–7.6 (m, Ph, 30 H), 4.24 (s, OMe, 3 H) and −19.25 [ddd, J(RhH) 14, J(Rh–PH) 4, J(Au–PH) 1.5, μ-H, 1 H]; ^{31}P, δ 27.2 [dd, J(RhP) 130, J(PP) 1] and 67.1 [dd, J(RhP) 5, J(PP) 1 Hz].

Compound **5**. IR: ν(CO)/cm^{-1} (cyclohexane) 2091w, 2069s, 2053w, 2039s, 2030vs, 2025vs, 2016vs, 1995m, 1975m, 1967m, 1940w and 1849w. The complex is unstable in solution at room temperature, so some weak bands may be due to small proportions of impurities. NMR ($CDCl_3$): ^{1}H, δ 7.2–7.6 (m, Ph, 30 H) and −17.37 (d, J 11, μ-H, 2 H); ^{31}P, δ 42.1 [d, J(RhP) 4] and 61.7 [d, J(RhP) 9 Hz].

X-Ray Crystallographic Studies.—Crystals were mounted in thin-wall glass capillaries and the crystal system and approximate cell dimensions established by preliminary photographic examination. The crystal density was measured by flotation in appropriate solvent mixtures. Intensity data were recorded at room temperature using an Enraf-Nonius CAD4 diffractometer equipped with Mo-Kα radiation (λ = 0.710 69 Å) and a graphite monochromator. Check reflections showed no significant decay with time during data collection for either of the studies. An empirical ψ-scan absorption correction was applied to each data set along with the Lorentz and polarisation correction.

The structures were solved using the Patterson strategy in SHELXS 86[10] to locate the heavy atoms followed by repeated structure-factor and difference electron-density syntheses. Structure refinement was carried out using SHELX 76[11] (full-matrix least squares for **3** or blocked full-matrix least-squares cycles for **4**) with minimisation of $\Sigma w(\Delta)^2$ in each case. Phenyl H atoms were placed in calculated positions [d(CH) = 0.95 Å] and given a common refined isotropic thermal parameter. Hydride atoms were located from difference electron-density syntheses towards the end of refinement and their positions refined with a fixed isotropic thermal parameter (0.08 Å^2). Scattering factors for neutral atoms and anomalous dispersion corrections were taken from SHELX 76 (P, O, N, C and H) and ref. 12 (Ru, Rh and Au). All calculations were carried out using an IBM 3090 computer, using the programs SHELXS 86,[10] SHELX 76,[11] and ORTEP II.[13]

$[Ru_3Rh_2H_2(CO)_{12}(PPh_3)_2]$ **3**. Suitable crystals of compound **3** were grown as air-stable, black plates by slow evaporation of a cyclohexane–CH_2Cl_2 solution at room temperature. Table 1 provides a summary of crystal data and structure-solution details. The data refined to a final R = 0.033 {anisotropic (Rh, Ru, P, O and C) and isotropic (H) atoms, $w = 1/[\sigma^2(F) + 0.0001F^2]$, maximum shift/error = 0.3}, with

Table 2 Atomic coordinates for $[Ru_3Rh_2H_2(CO)_{12}(PPh_3)_2]$ **3**

Atom	*x*	*y*	*z*
Ru(1)	0.000 00	0.628 88(6)	0.250 00
Ru(2)	0.677 1(2)	0.355 07(4)	0.243 55(1)
Rh(1)	0.030 75(2)	0.462 07(4)	0.338 51(1)
P(1)	0.121 41(6)	0.554 92(12)	0.405 50(4)
C(1)	−0.067 9(3)	0.767 2(6)	0.228 0(2)
O(1)	−0.109 1(3)	0.847 6(5)	0.216 9(2)
C(2)	−0.036 4(3)	0.617 5(5)	0.321 4(2)
O(2)	−0.077 4(2)	0.669 0(4)	0.339 6(1)
C(3)	−0.007 4(3)	0.372 2(5)	0.387 3(2)
O(3)	−0.030 1(2)	0.320 2(5)	0.418 3(2)
C(4)	0.150 7(3)	0.396 0(6)	0.217 6(2)
O(4)	0.199 7(2)	0.414 8(6)	0.201 8(2)
C(5)	0.119 8(3)	0.266 1(6)	0.304 8(2)
O(5)	0.154 8(2)	0.201 7(5)	0.336 5(2)
C(6)	0.041 9(3)	0.192 3(6)	0.207 8(2)
O(6)	0.027 5(2)	0.088 6(5)	0.189 0(2)
C(11)	0.211 5(2)	0.567 0(5)	0.395 7(2)
C(12)	0.268 1(3)	0.591 9(5)	0.437 4(2)
C(13)	0.336 0(3)	0.599 4(6)	0.430 3(2)
C(14)	0.348 5(3)	0.577 3(7)	0.381 9(2)
C(15)	0.293 4(3)	0.555 4(8)	0.339 5(2)
C(16)	0.224 7(3)	0.550 8(7)	0.346 4(2)
C(21)	0.137 3(2)	0.466 5(5)	0.468 5(2)
C(22)	0.143 0(3)	0.529 4(6)	0.516 3(2)
C(23)	0.159 7(4)	0.457 1(8)	0.562 4(2)
C(24)	0.170 0(3)	0.320 3(7)	0.561 6(2)
C(25)	0.165 1(3)	0.257 4(6)	0.514 7(2)
C(26)	0.149 2(3)	0.328 6(5)	0.468 2(2)
C(31)	0.098 5(3)	0.725 5(5)	0.420 9(2)
C(32)	0.036 1(3)	0.745 0(6)	0.437 3(2)
C(33)	0.013 7(3)	0.874 4(7)	0.445 4(2)
C(34)	0.053 2(4)	0.983 5(7)	0.437 1(2)
C(35)	0.114 9(4)	0.963 9(6)	0.420 7(2)
C(36)	0.137 9(3)	0.835 8(5)	0.412 8(2)
H(1)	0.068 9(32)	0.500 7(66)	0.282 4(23)

Table 3 Atomic coordinates for $[Ru_3RhAuH(CO)_{10}(PPh_3)_2(\mu_3\text{-}COMe)]$ **4**

Atom	*x*	*y*	*z*
Au	0.236 00(3)	0.064 59(2)	0.262 36(2)
Rh	0.300 70(5)	−0.153 03(4)	0.234 05(3)
Ru(1)	0.368 67(6)	−0.274 05(4)	0.373 64(3)
Ru(2)	0.447 21(6)	−0.086 89(4)	0.308 68(3)
Ru(3)	0.197 78(6)	−0.082 47(4)	0.404 78(3)
P(1)	0.175 5(2)	0.237 9(1)	0.199 3(1)
P(2)	0.147 5(2)	−0.196 2(1)	0.194 3(1)
C(1)	0.358 3(8)	−0.089 3(6)	0.128 1(5)
O(1)	0.397 7(6)	−0.053 9(4)	0.060 0(3)
C(2)	0.477 3(7)	0.013 5(6)	0.206 0(5)
O(2)	0.518 9(6)	0.067 2(5)	0.147 2(4)
C(3)	0.599 3(7)	−0.181 7(6)	0.281 6(4)
O(3)	0.692 4(5)	−0.239 3(5)	0.264 6(4)
C(4)	0.511 1(9)	−0.018 5(7)	0.364 8(5)
O(4)	0.553 0(9)	0.019 8(7)	0.398 1(5)
C(5)	0.202 8(8)	0.020 0(6)	0.457 7(5)
O(5)	0.212 8(6)	0.076 6(5)	0.491 6(4)
C(6)	0.047 4(8)	−0.007 3(6)	0.357 3(5)
O(6)	−0.049 8(6)	0.030 2(4)	0.342 5(3)
C(7)	0.105 2(8)	−0.159 7(6)	0.500 0(5)
O(7)	0.051 0(6)	−0.205 3(5)	0.554 9(4)
C(8)	0.271 8(8)	−0.368 6(6)	0.436 9(5)
O(8)	0.210 9(7)	−0.422 6(5)	0.478 2(4)
C(9)	0.508 1(9)	−0.368 5(7)	0.411 3(6)
O(9)	0.593 0(7)	−0.424 3(6)	0.432 6(5)
C(10)	0.418 4(7)	−0.301 5(5)	0.254 3(4)
O(10)	0.483 7(5)	−0.357 7(4)	0.212 9(3)
C(11)	0.372 7(7)	−0.164 2(6)	0.429 6(4)
O(11)	0.424 3(6)	−0.173 5(4)	0.495 7(3)
C(12)	0.365 1(11)	−0.219 4(9)	0.575 4(5)
C(21)	0.263 1(7)	0.308 4(6)	0.230 1(4)
C(22)	0.261 6(9)	0.289 9(7)	0.315 6(5)
C(23)	0.325 9(9)	0.340 3(7)	0.343 5(6)
C(24)	0.387 9(9)	0.410 1(7)	0.289 7(5)
C(25)	0.391 4(9)	0.426 9(7)	0.206 8(5)
C(26)	0.328 7(8)	0.378 4(6)	0.175 2(5)
C(31)	0.012 0(7)	0.305 7(5)	0.227 4(4)
C(32)	−0.080 4(8)	0.262 6(6)	0.221 5(5)
C(33)	−0.205 3(10)	0.316 3(7)	0.235 4(5)
C(34)	−0.237 1(10)	0.411 2(7)	0.258 7(6)
C(35)	−0.149 5(9)	0.451 8(8)	0.267 4(6)
C(36)	−0.021 7(8)	0.401 3(6)	0.250 7(5)
C(41)	0.203 1(7)	0.274 5(5)	0.086 4(4)
C(42)	0.287 4(8)	0.206 2(7)	0.039 7(5)
C(43)	0.307 2(9)	0.232 6(7)	−0.044 8(6)
C(44)	0.249 2(8)	0.325 8(6)	−0.085 2(5)
C(45)	0.164 9(9)	0.393 2(7)	−0.040 3(5)
C(46)	0.141 4(9)	0.367 6(7)	0.046 3(5)
C(51)	0.029 2(7)	−0.088 7(5)	0.151 0(4)
C(52)	0.054 5(7)	0.009 1(6)	0.117 8(4)
C(53)	−0.033 0(8)	0.088 9(7)	0.081 0(5)
C(54)	−0.144 9(9)	0.075 4(7)	0.078 3(5)
C(55)	−0.169 8(10)	−0.019 6(7)	0.109 7(5)
C(56)	−0.084 7(8)	−0.103 2(7)	0.147 9(5)
C(61)	0.204 9(7)	−0.275 7(5)	0.114 6(4)
C(62)	0.124 1(8)	−0.316 9(6)	0.093 3(5)
C(63)	0.168 8(9)	−0.369 6(7)	0.027 9(5)
C(64)	0.287 5(9)	−0.381 6(7)	−0.011 2(5)
C(65)	0.369 3(9)	−0.344 3(7)	0.009 1(5)
C(66)	0.328 6(8)	−0.288 8(6)	0.072 5(5)
C(71)	0.056 6(7)	−0.271 1(5)	0.279 9(4)
C(72)	0.091 0(8)	−0.379 5(6)	0.299 1(5)
C(73)	0.023 4(8)	−0.434 1(7)	0.368 8(5)
C(74)	−0.076 4(9)	−0.382 8(7)	0.417 1(5)
C(75)	−0.113 6(8)	−0.275 3(6)	0.400 7(5)
C(76)	−0.045 9(8)	−0.219 7(6)	0.330 9(5)
H(1)	0.230 3(74)	−0.169 4(57)	0.321 9(45)

the residual electron density in the range 1.24 to −0.80 e Å^{-3}. The Rh atoms were distinguished from Ru by $^{31}P-\{^{1}H\}$ NMR spectroscopy which showed $^{1}J(RhP)$ coupling in solution. The final atomic coordinates are given in Table 2.

$[Ru_3RhAuH(CO)_{10}(PPh_3)_2(\mu_3\text{-}COMe)]$ **4**. Suitable crystals of compound **4** were grown as red rectangular plates by slow evaporation of a hexane–CH_2Cl_2 solution at room temperature. Table 1 provides a summary of crystal data and structure solution details. The data refined to a final $R = 0.037$ {anisotropic [Au, Rh, Ru, P, O and C (carbonyl and COMe)] and [C(phenyl), H] isotropic atoms, $w = 1/[\sigma^2(F) + 0.0002F^2]$, maximum shift/error = 0.2}, with the residual electron density in the range 0.85 to −0.93 e Å^{-3}. The Rh atoms were distinguished from Ru by $^{31}P-\{^{1}H\}$ NMR spectroscopy which showed $^{1}J(RhP)$ coupling in solution. The final atomic coordinates are given in Table 3.

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

Results and Discussion

Synthesis of $[Ru_3Rh_2H_2(CO)_{12}(PPh_3)_2]$ **3**.—Treatment of the anionic mixture generated by the reaction of $K[BHBu^{s}_{3}]$

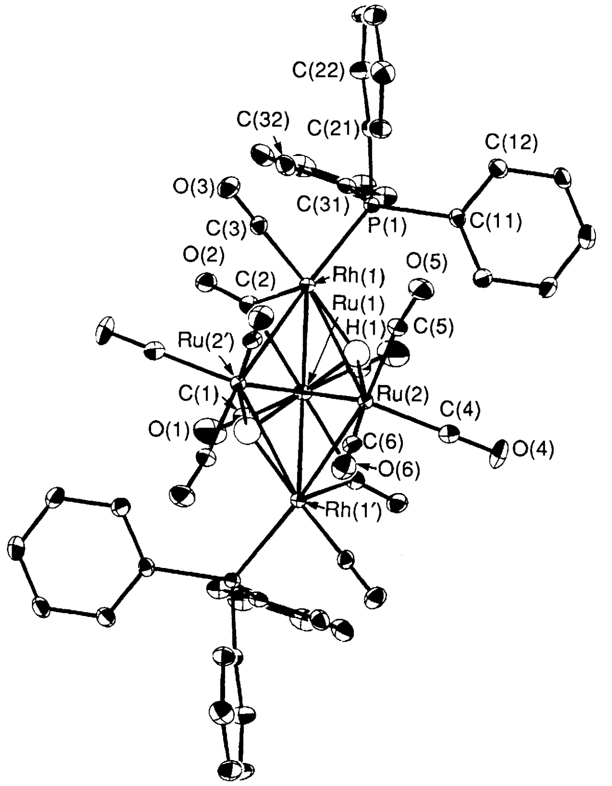


Fig. 1 The molecular structure of $[Ru_3Rh_2H_2(CO)_{12}(PPh_3)_2]$ **3** showing the atom labelling scheme. Phenyl H atoms have been omitted for clarity and the thermal ellipsoids have been drawn at the 20% probability level

Table 4 Selected bond distances (Å) and angles (°) for $[Ru_3Rh_2H_2(CO)_{12}(PPh_3)_2]$ **3**

Ru(1)–Ru(2)	3.045(1)	Rh(1)–P(1)	2.365(1)
Ru(1)–Rh(1)	2.798(1)		
Rh(1)–Ru(2)	2.939(1)	Ru(1)–H(1)	1.90(6)
Ru(2)–Ru(2′)	2.726(1)	Ru(2)–H(1)	1.77(6)
Rh(1)–Ru(2′)	2.738(1)	Rh(1)–H(1)	1.83(6)
Ru(1)–C(1)	1.899(6)	Ru(2)–C(5)	1.903(5)
Ru(1)–C(2)	2.146(5)	Ru(2)–C(6)	1.878(6)
Rh(1)–C(2)	2.005(5)	P(1)–C(11)	1.829(5)
Rh(1)–C(3)	1.846(5)	P(1)–C(21)	1.830(5)
Ru(2)–C(4)	1.929(6)	P(1)–C(31)	1.822(5)
C–O (carbonyl)	min. 1.121(7)	max. 1.149(7)	
C–C (phenyl)	min. 1.360(8)	max. 1.391(7)	
Ru(1)–Rh(1)–Ru(2)	64.1(1)	Ru(2′)–Ru(2)–Rh(1)	57.7(1)
Rh(1)–Ru(2)–Ru(1)	55.7(1)	Ru(2)–Rh(1)–Ru(2′)	57.3(1)
Ru(2)–Ru(1)–Rh(1)	60.2(1)	Rh(1)–Ru(2′)–Ru(2)	65.1(1)
Ru(1)–Rh(1)–Ru(2′)	66.7(1)	Ru(2)–Ru(1)–Ru(2′)	53.2(1)
Rh(1)–Ru(2′)–Ru(1)	57.6(1)	Ru(1)–Ru(2)–Ru(2′)	63.4(1)
Ru(2′)–Ru(1)–Rh(1)	55.7(1)		
Ru(1)–C(2)–O(2)	138.0(4)	Rh(1)–C(2)–O(2)	137.2(4)
Rh(1)–P(1)–C(11)	119.6(2)	C(11)–P(1)–C(21)	101.0(2)
Rh(1)–P(1)–C(21)	114.9(1)	C(21)–P(1)–C(31)	104.3(2)
Rh(1)–P(1)–C(31)	110.4(1)	C(31)–P(1)–C(11)	105.1(2)
Ru/Rh–C–O (terminal)	min. 170.0(5)	max. 177.8(5)	
C–C–C (phenyl)	min. 118.2(5)	max. 121.1(5)	

Symmetry code: (′) $-x, y, \frac{1}{2} - z$.

and $[Ru_3RhH_2(CO)_{10}(PPh_3)(\mu\text{-}COMe)]$ **2** (in thf) with an equimolar quantity of $[Rh(CO)_3(PPh_3)_2]^+$ leads to no reaction. However, if the thf is removed after generating the anionic mixture and the reaction with $[Rh(CO)_3(PPh_3)_2]^+$ is carried out in CH_2Cl_2 the pentanuclear cluster $[Ru_3Rh_2H_2(CO)_{12}(PPh_3)_2]$ **3** is generated in 29% yield. The need to change solvent to achieve reaction suggests that the anion giving rise to **3** is considerably stabilised by thf and that the use of a weakly co-ordinating solvent (CH_2Cl_2) increases its reactivity substantially. Also generated in this reaction is a small quantity of $[Ru_3RhH_2(CO)_9(PPh_3)_2(\mu\text{-}COMe)]$.

The X-Ray Structure of $[Ru_3Rh_2H_2(CO)_{12}(PPh_3)_2]$ **3**.—The structure consists of discrete molecules in which each molecule of compound **3** adopts a distorted trigonal-bipyramidal metal core (as expected for a 72-valence-electron cluster).[14] The molecule is shown in Fig. 1 and the bond lengths and angles are presented in Table 4. The molecule has crystallographic C_2 symmetry with the three Ru atoms in the equatorial positions and the two Rh atoms in the axial positions. There are 10 terminal and two bridging carbonyl groups. The bridging CO [C(2)–O(2)] spans the Ru(1)–Rh(1) distance in an unsymmetrical manner [Ru(1)–C(2) 2.146(5), Rh(1)–C(2) 2.005(5) Å]; this arrangement might be expected as the Rh is formally electron poor and the Ru electron rich. The triphenylphosphine lies in a position to cover the Ru(1)–Ru(2)–Rh(1) face and it is just this face that is occupied by the hydride using the space 'created' by the steric bulk of the phosphine. The same effect has been noted[6] for $[Ru_3RhH_2(CO)_{10}(PPh_3)(\mu\text{-}COMe)]$ **2**. The three metal–hydride bond lengths are similar (*ca.* 1.8 Å) and do not differ from values determined for edge-bridging hydrides.[15] The metal cluster and the bridging ligands are shown more clearly in Fig. 2. The terminal CO groups are essentially linear except for C(5)–O(5) [Ru(2)–C(5)–O(5) 170.0(5)°] which semibridges to Rh(1) [Rh(1) ··· C(5) 2.875(6) Å]. Again this interaction can be accounted for by the electron deficiency of Rh(1).

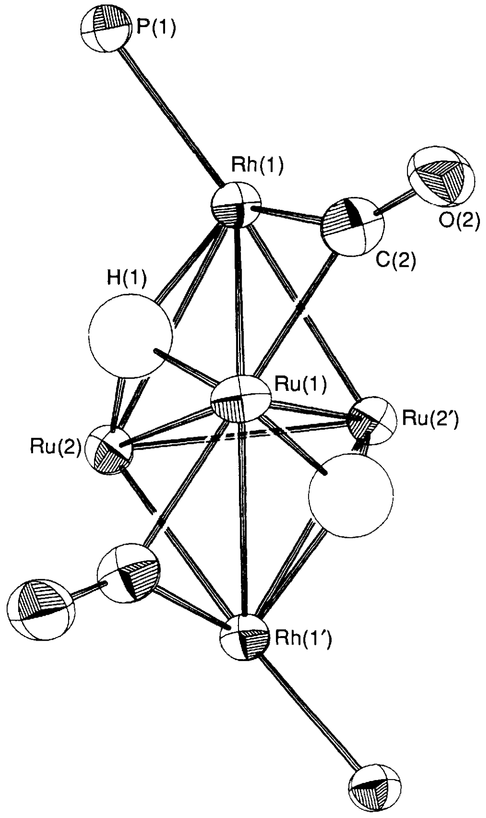


Fig. 2 The metal core, phosphorus atoms and bridging ligands in $[Ru_3Rh_2H_2(CO)_{12}(PPh_3)_2]$ **3**. Thermal ellipsoids drawn at the 50% probability level. Symmetry code: (′) $-x, y, \frac{1}{2} - z$

Spectroscopic Characterisation of $[Ru_3Rh_2H_2(CO)_{12}(PPh_3)_2]$ **3**.—The ^1H NMR spectrum of compound **3** at 253 K

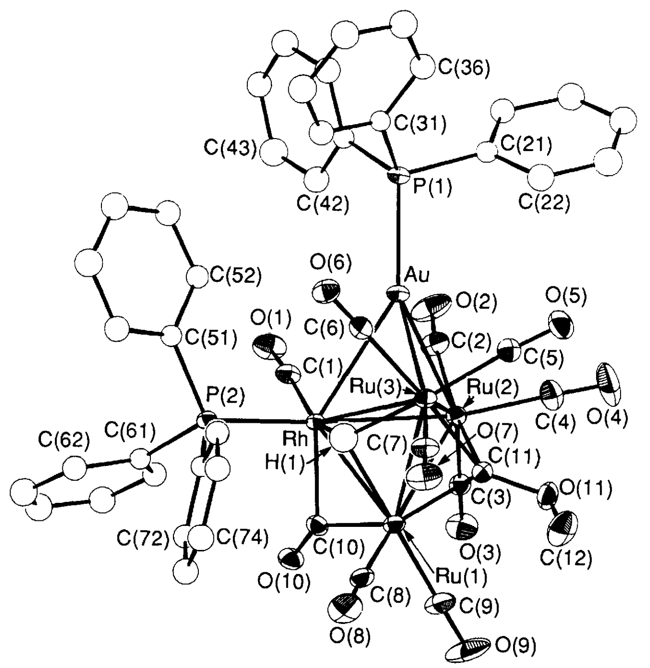


Fig. 3 The molecular structure of $[Ru_3RhAuH(CO)_{10}(PPh_3)_2(\mu_3\text{-COMe})]$ **4** showing the atom labelling scheme. Phenyl H atoms have been omitted for clarity and the thermal ellipsoids have been drawn at the 20% probability level

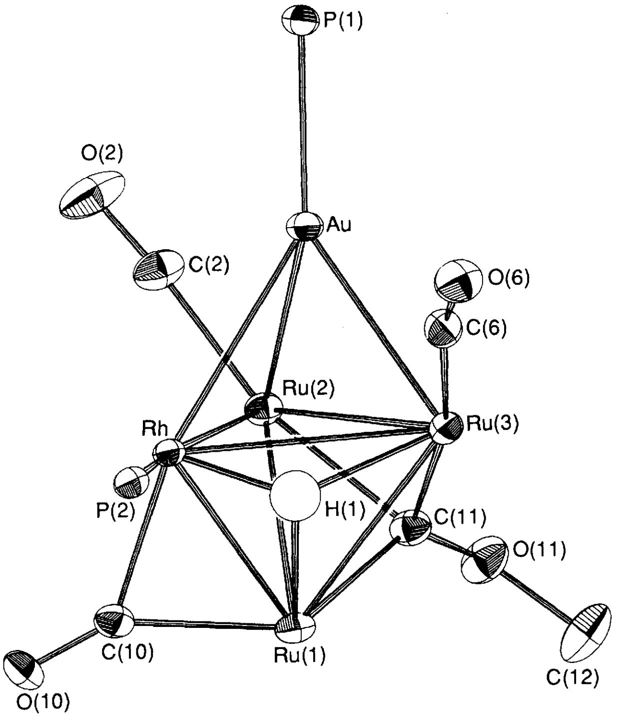


Fig. 4 The metal core, phosphorus atoms, bridging ligands and semi-bridging CO groups of $[Ru_3RhAuH(CO)_{10}(PPh_3)_2(\mu_3\text{-COMe})]$ **4**

(CD_2Cl_2, 360.14 MHz) includes a doublet of triplets (J = 15, 3.5 Hz) at δ −19.36 due to the hydrides. At 333 K ($CDCl_3$, 89.55 MHz) the hydride signal appears as illustrated in Fig. 5 which is interpreted as a triplet of triplets with coupling constants of 7 and 3.5 Hz. The calculated multiplet arising from a triplet of triplets with these couplings is a seven-line spectrum with intensity ratio 1:2:3:4:3:2:1 which is consistent with the observed signal. The change observed for the hydride signal on warming from 253 to 333 K is accounted for by the onset of hydride exchange. At 253 K (hydrides static) the larger coupling (15 Hz) is assigned as ^1J(RhH) with the triplet coupling (3.5 Hz) arising from equal coupling to the two phosphorus nuclei. Under conditions of rapid exchange these assignments lead to a predicted triplet of triplets hydride signal with an averaged coupling to the two Rh nuclei of 7.5 Hz and an averaged coupling to the two phosphorus nuclei of 3.5 Hz (as observed). Heating to 373 K ([$^2H_8$]toluene) leads to no further change in the structure of the hydride signal.

The CO signals in the $^{13}C\text{-}\{^1H\}$ NMR spectrum ($CDCl_3$, 223 K) are illustrated in Fig. 6 along with a schematic representation of a molecule of **3**. The molecular symmetry of **3** predicts six pairs of inequivalent CO ligands and consistent with this six signals of equal intensity are observed. The doublet signal at δ 225.5 is assigned to the bridging CO, labelled b, with the coupling of 44 Hz attributed to $^{103}Rh\text{–}^{13}C$ coupling. The ion $[RuRh_4(CO)_{15}]^{2-}$ also has a pair of CO groups that asymmetrically bridge a Ru–Rh bond such that the bonding to Rh is stronger and these show a similar RhC coupling (36 Hz).[16] The doublet of doublets signal for **3** (δ 190.4) is assigned to the Rh-bound terminal CO, labelled c, with the larger coupling (85 Hz) typical for a ^1J(RhC) interaction and the smaller coupling (15 Hz) attributed to ^2J(PC). The remaining four signals are due to the four pairs of terminal CO groups labelled a, d, e and f where one of these shows a small coupling [^2J(RhC) or ^3J(PC)] of 11 Hz.

The Reactivity of Compound **3**.—(*a*) *With* CO. Bubbling CO through a thf solution of compound **3** at room temperature leads to rapid cluster disintegration (IR spectroscopy shows that no **3** is left after 65 min). TLC (using light petroleum ether–CH_2Cl_2, 3:1 v/v) shows about five products along with a significant stationary residue. The major product separated was shown to be the previously reported[17] $[Ru_3(CO)_{11}(PPh_3)]$.

(*b*) *Attempted deprotonation*. Infrared studies show that a thf solution of compound **3** reacts with an equivalent of $K[BHBu^s_3]$ to regenerate the anion $[Ru_3RhH_2(CO)_{11}(PPh_3)]^-$. Similar heterometal decapping was also observed for attempted deprotonation of $[Ru_3RhH(CO)_{10}(PEt_3)(\mu_3\text{-PPh})]$ with methanolic KOH where the major product was the anion $[Ru_3H(CO)_9(\mu_3\text{-PPh})]^-$.[18]

The Heterometallic Clusters $[Ru_3RhAuH(CO)_{10}(PPh_3)_2(\mu_3\text{-COMe})]$ **4** *and* $[Ru_3RhAuH_2(CO)_{11}(PPh_3)_2]$ **5**.—In a similar fashion to that observed for the reactivity of $[Rh(CO)_3(PPh_3)_2]^+$ in the formation of compound **3**, the anionic mixture generated by the reaction of **2** with $K[BHBu^s_3]$ shows no reaction with $[Au(PPh_3)Cl]$ using thf as the solvent. However, a change of solvent to CH_2Cl_2 after creation of the anionic mixture and treatment with $[Au(PPh_3)Cl]$ leads to formation of the two clusters $[Ru_3RhAuH(CO)_{10}(PPh_3)_2(\mu_3\text{-COMe})]$ **4** and $[Ru_3RhAuH_2(CO)_{11}(PPh_3)_2]$ **5** in yields of 5 and 19% respectively.

The X-Ray Structure of $[Ru_3RhAuH(CO)_{10}(PPh_3)_2(\mu_3\text{-COMe})]$ **4**.—The structure consists of discrete molecules based on a distorted trigonal-bipyramidal metal core Ru_3RhAu; one molecule is shown in Fig. 3 and in Table 5 are presented some bond lengths and angles. Two Ru atoms and one Rh atom define the equatorial plane of the trigonal-bipyramidal unit with axial Ru and Au atoms. Among the ten carbonyl groups, there are seven terminal, one bridging, and two semibridging. The bridging carbonyl [C(10)–O(10)] symmetrically spans the Ru(1)–Rh edge and is associated with the longest Ru–C distance. The next two longest Ru–C distances [to C(2) and C(6)] have a semibridging relation to Au [Au ··· C(2) 2.604(8), Au ··· C(6) 2.592(8) Å] and in agreement with this are associated with non-linear Ru–C–O angles [168°(av.)] (see Fig. 4). The rhodium atom was identified on the basis of solution NMR data and is bonded to P(2), while the gold atom is bonded to P(1). The cluster geometry is completed by a face-

Table 5 Selected bond distances (Å) and angles (°) for $[Ru_3RhAuH(CO)_{10}(PPh_3)_2(\mu_3\text{-}COMe)]$ **4**

Ru(1)–Ru(2)	2.811(1)	P(1)–Au	2.312(2)	Ru(2)–C(3)	1.868(7)	Ru(1)–C(9)	1.869(9)
Ru(1)–Ru(3)	2.867(1)	P(2)–Rh	2.302(2)	Ru(2)–C(4)	1.897(12)	Ru(1)–C(10)	2.079(8)
Ru(2)–Ru(3)	2.867(1)	H(1)–Rh	1.50(7)	Ru(3)–C(5)	1.892(10)	Rh–C(10)	2.083(7)
Ru(1)–Rh	2.671(1)	H(1)–Ru(1)	2.01(7)	Ru(3)–C(6)	1.974(9)	Ru(3)–C(11)	2.068(8)
Ru(2)–Rh	2.807(1)	H(1)–Ru(3)	1.99(9)	Ru(1)–C(11)	2.013(9)	P(2)–C(51)	1.820(7)
Ru(3)–Rh	3.150(1)	C(11)–O(11)	1.37(1)	Ru(2)–C(11)	2.127(7)	P(2)–C(61)	1.845(7)
Rh–Au	3.007(1)	O(11)–C(12)	1.41(1)	P(1)–C(21)	1.825(7)	P(2)–C(71)	1.809(7)
Ru(2)–Au	2.813(1)	Ru(3)–C(7)	1.921(7)	P(1)–C(31)	1.818(7)	Au···C(6)	2.592(8)
Ru(3)–Au	2.735(1)	Ru(1)–C(8)	1.873(9)	P(1)–C(41)	1.824(7)	Au···C(2)	2.604(8)
Rh–C(1)	1.823(7)						
Ru(2)–C(2)	1.935(8)						
C–O (carbonyl)	min. 1.12(1)	max. 1.16(1)		C–C (phenyl)	min. 1.32(1)	max. 1.41(1)	
Ru(1)–Ru(2)–Ru(3)	60.6(1)	Ru(2)–Rh–Ru(3)	57.2(1)	Au–P(1)–C(21)	106.9(2)	C(21)–P(1)–C(31)	104.3(3)
Ru(2)–Ru(3)–Ru(1)	58.7(1)	Rh–Ru(2)–Au	64.7(1)	Au–P(1)–C(31)	118.1(2)	C(31)–P(1)–C(41)	101.5(3)
Ru(3)–Ru(1)–Ru(2)	60.6(1)	Ru(2)–Au–Rh	57.6(1)	Au–P(1)–C(41)	119.0(2)	C(41)–P(1)–C(21)	105.5(3)
Ru(1)–Rh–Ru(2)	61.7(1)	Au–Rh–Ru(2)	57.8(1)	Rh–P(2)–C(51)	116.7(2)	C(51)–P(2)–C(61)	102.7(3)
Rh–Ru(2)–Ru(1)	56.8(1)	Rh–Ru(3)–Au	61.0(1)	Rh–P(2)–C(61)	115.4(2)	C(61)–P(2)–C(71)	104.6(3)
Ru(2)–Ru(1)–Rh	61.5(1)	Ru(3)–Au–Rh	66.4(1)	Rh–P(2)–C(71)	112.2(2)	C(71)–P(2)–C(51)	103.8(3)
Ru(1)–Rh–Ru(3)	58.3(1)	Au–Rh–Ru(3)	52.7(1)	Ru(1)–C(11)–O(11)	130.0(5)	Ru(1)–C(11)–Ru(2)	85.5(3)
Rh–Ru(3)–Ru(1)	52.5(1)	Ru(3)–Ru(2)–Au	57.6(1)	Ru(2)–C(11)–O(11)	121.1(6)	Ru(2)–C(11)–Ru(3)	86.2(3)
Ru(3)–Ru(1)–Rh	69.2(1)	Ru(2)–Au–Ru(3)	62.2(1)	Ru(3)–C(11)–O(11)	130.1(5)	Ru(3)–C(11)–Ru(1)	89.2(4)
Rh–Ru(3)–Ru(2)	55.4(1)	Au–Ru(3)–Ru(2)	60.2(1)	C(11)–O(11)–C(12)	118.3(8)	Ru(2)–C(2)–O(2)	166.7(8)
Ru(3)–Ru(2)–Rh	67.4(1)	P(2)–Rh–Ru(1)	115.0(1)	Rh–C(10)–O(10)	135.6(6)	Ru(3)–C(6)–O(6)	168.8(6)
P(1)–Au–Rh	143.0(1)	P(2)–Rh–Ru(2)	168.2(1)	Ru(1)–C(10)–O(10)	144.1(6)		
P(1)–Au–Ru(2)	141.4(1)	P(2)–Rh–Ru(3)	111.1(1)				
P(1)–Au–Ru(3)	145.1(1)	P(2)–Rh–Au	115.2(1)				
Ru/Rh–C–O (terminal)	min. 166.7(8)	max. 179.6(4)		C–C–C (phenyl)	min. 118.1(8)	max. 122.5(9)	

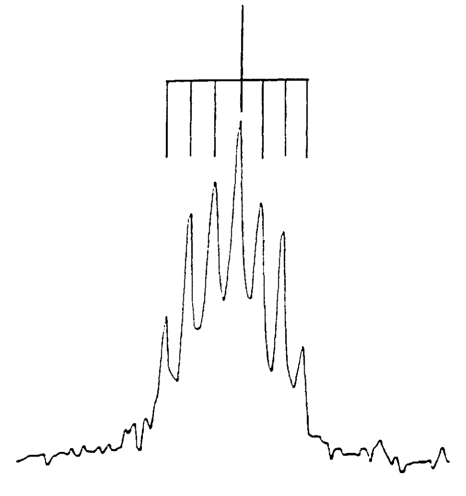


Fig. 5 The hydride resonance in the ^1H NMR spectrum of compound 3 (333 K, $CDCl_3$, 89.55 MHz)

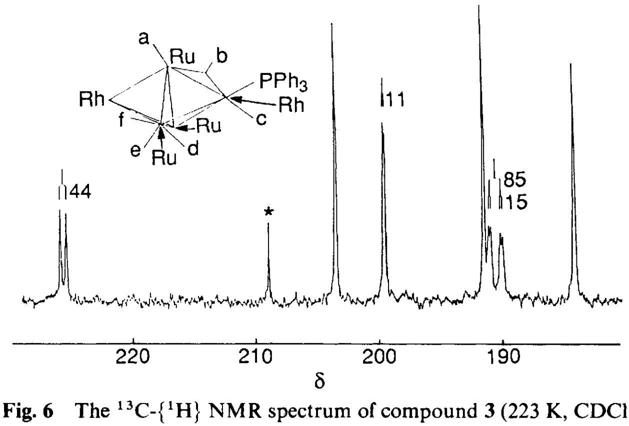


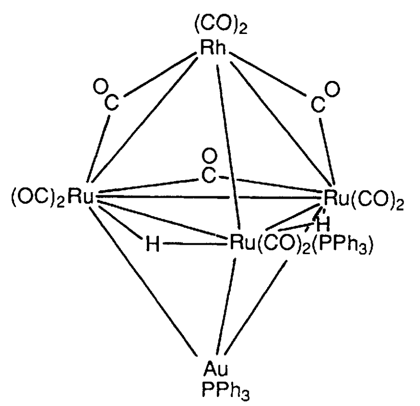
Fig. 6 The $^{13}C\text{-}\{^1H\}$ NMR spectrum of compound 3 (223 K, $CDCl_3$, 90.55 MHz) in the CO region. The asterisk indicates an impurity

capping (μ_3) hydrido and a μ_3-COMe ligand (Fig. 4). The COMe group rather unsymmetrically bridges the Ru_3 face and the Ru(2)–C(11)–O(11)–C(12) unit is nearly planar (torsion angle 176°).

The structure of compound **4** can be compared to $[Au_2Ru_3(CO)_9(PPh_3)_2(\mu_3\text{-}S)]$ which also contains a trigonal-bipyramidal metal core with an axial and equatorial Au atom.[19] The μ_3-S capping ligand bonds to three Ru atoms. The structure of $[Au_2Ru_3(CO)_8(PPh_3)_3(\mu_3\text{-}S)]$ has also been determined[20] and is similar. A face-capping COMe group has been found[20] in $[Au_2Ru_3H(CO)_9(PPh_3)_2(\mu_3\text{-}COMe)]$ and shows a similar geometry, however the Au_2Ru_3 cluster adopts a square-pyramidal ('*nido*') geometry with an apical Ru atom and the COMe group capping a Ru_3 triangular face. Compound **4** and both the Au_2Ru_3 clusters have polyhedral electron counts of 72 electrons with the '*nido*' structure of the last example violating the theoretical prediction.[14] The core structure of **4** is also similar to that of $[AuCoRu_3(CO)_{13}(PPh_3)]$ where the Au atom caps the heterometallic Ru_2Co face.[21]

Spectroscopic Characterisation of $[Ru_3RhAuH_2(CO)_{11}(PPh_3)_2]$ **5**.—The ^1H NMR spectrum shows phenyl signals due to the PPh_3 ligands and a doublet hydride signal at δ −17.37 with a coupling of 11 Hz. The $^{31}P\text{-}\{^1H\}$ NMR spectrum shows the PPh_3 ligands are bound to Au and Ru (signals at δ 61.7 and 42.1 respectively) with the coupling shown for each signal (9 and 4 Hz respectively) attributed to ^2J(RhP). Unfortunately no further structural information could be obtained from the $^{13}C\text{-}\{^1H\}$ NMR spectrum which at 183 K (CD_2Cl_2) shows a very broad signal (δ ≈ 195) for the CO ligands indicating the presence of slow exchange.

The formulation of **5** is based on the assumption that it results from reaction of $[Au(PPh_3)Cl]$ with the anion $[Ru_3RhH_2(CO)_{11}(PPh_3)]^-$ {generated by loss of the Me group from $[Ru_3RhH_2(CO)_{10}(PPh_3)(\mu\text{-}COMe)]$ **2**}. Consideration of (*a*) the metal-core structure of **3** {also formed from $[Ru_3RhH_2(CO)_{11}(PPh_3)]^-$ and with the second heterometal capping a Ru_3 face}, (*b*) the structure[6] of $[Ru_3RhH_2(CO)_{11}(PPh_3)]^-$ and (*c*) the structure of **4** results in the predicted structure for **5**. Alternative structures could be



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envisaged with the $AuPPh_3$ unit edge-bridging and, although this would be inconsistent with the polyhedral electron count, such structures are known,[5] *e.g.* $[Ru_4H_3(CO)_{12}(AuPPh_3)]$. The coupling (11 Hz) observed for the hydrides in the ^1H NMR spectrum of compound **5** is very similar to that for the hydrides of $[N(PPh_3)_2][Ru_3RhH_2(CO)_{11}(PPh_3)]$ and hence it seems reasonable that they occupy the same relative positions on the Ru_3Rh unit. For both, the coupling is attributed to a $^2J(PH)$ interaction.

Conclusion

The anionic mixture generated by treatment of compound **2** with $K[BHBu^s_3]$ in thf reacts with $[Rh(CO)_3(PPh_3)_2]^+$ or $[Au(PPh_3)Cl]$ to generate the pentanuclear heterometallic clusters **3**–**5**. The products **3** and **5** are believed to be derived from the anion $[Ru_3RhH_2(CO)_{11}(PPh_3)]^-$ while **4** is thought to result from the anion $[Ru_3RhH(CO)_{10}(PPh_3)(COMe)]^-$. A Ru_3Rh_2 cluster analogous to **4**, that is with the COMe ligand intact, was not isolated.

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