Ruthenium Carbonyl Cluster Complexes with Oxygen Ligands. Part 2.[1] Auration of a Hexaruthenium 'Raft' Cluster; Crystal Structures of $[Ru_6(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}O{:}\mu\text{-}C{:}\eta^6\text{-}OC_6H_3OMe\text{-}4)(CO)_{16}]$ and $[AuRu_6(\mu_3\text{-}H)(\mu\text{-}O{:}\mu\text{-}C{:}\eta^6\text{-}OC_6H_3OMe\text{-}4)(CO)_{16}(PPh_3)]$†

Marie P. Cifuentes,[a] Tyrone P. Jeynes,[a] Mark G. Humphrey,[*,a] Brian W. Skelton[b] and Allan H. White[b]
[a] *Department of Chemistry, University of New England, Armidale, New South Wales 2351, Australia*
[b] *Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6009, Australia*

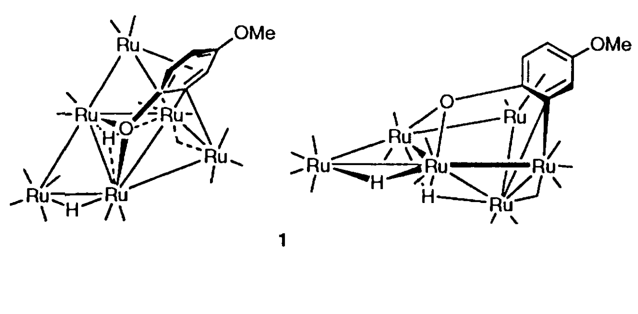
The hexaruthenium raft cluster $[Ru_6(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}O{:}\mu\text{-}C{:}\eta^6\text{-}OC_6H_3OMe\text{-}4)(CO)_{16}]$ **1** is smoothly deprotonated by K-Selectride {K[B(CHMeEt)$_3$H] in tetrahydrofuran}, the resulting cluster anion being aurated by $[AuCl(PPh_3)]$ to afford the mixed-metal cluster $[AuRu_6(\mu_3\text{-}H)(\mu\text{-}O{:}\mu\text{-}C{:}\eta^6\text{-}OC_6H_3OMe\text{-}4)(CO)_{16}(PPh_3)]$ **2** as the major product in moderate yield. The crystal structures of both **1** and **2** have been determined. The structural studies have revealed that isostructural replacement of H by isolobal Au(PPh$_3$) has not occurred; rather, an edge-bridging hydride has been replaced by a face-capping (phosphine)aurio moiety. In an analogous fashion to the auration, sequential reaction of **1** with K-Selectride and H_3PO_4 regenerated **1**. By contrast, hydrogenation [1 atm (*ca.* 10^5Pa) H_2, refluxing cyclohexane] of **1** resulted in expulsion of the $^-OC_6H_3OMe\text{-}4$ ligand and formation of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$.

We have been examining the reactivity of ruthenium clusters with N- and O-donor ligands[1–3] in order to model the hydrotreating of coal-derived fuels, and have recently described the synthesis of the (hydrido)ruthenium 'raft' cluster $[Ru_6(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}O{:}\mu\text{-}C{:}\eta^6\text{-}OC_6H_3OMe\text{-}4)(CO)_{16}]$ **1**, formed as two isomers (ratio 2:1) from reaction between $[Ru_3(CO)_{12}]$ and 4-methoxyphenol in refluxing cyclohexane.[1] An X-ray structural study on the phenol-derived analogue $[Ru_6(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}O{:}\mu\text{-}C{:}\eta^6\text{-}OC_6H_4)(CO)_{16}]$ **3** showed that the resultant raft cluster contains a $^-OC_6H_4$ ligand co-ordinated parallel to the pentaruthenium plane,[4] a co-ordination mode similar to that shown by scanning tunneling microscopy for phenol on $TiO_2(111)$.[5] The close structural analogy here prompted us to examine these species as model hydrotreating intermediates for the deoxygenation of phenols. We herein report the results of treating **1** with molecular hydrogen, H^-/H^+, and isolobal $H^-/Au(PPh_3)^+$, which might be expected to model the hydrotreating of absorbed phenols.

Results and Discussion

Synthesis and Characterization.—Bubbling hydrogen gas through a refluxing solution of **1** in an attempt to reduce the 4-methoxyphenol-derived ligand afforded the known (hydrido)-cluster carbonyl $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$; no evidence for any reaction intermediate by solution IR monitoring was found, either under these conditions or at lower temperatures. Bhaduri *et al.*[6] have reported that carbonylation of **3** similarly led to expulsion of the $^-OC_6H_4$, $[Ru_3(CO)_{12}]$ being the only characterized reaction product. With these results in mind, controlled addition of H_2 by sequential treatment of **1** with K-Selectride {K[B(CHMeEt)$_3$H] in tetrahydrofuran (thf)} and H_3PO_4 was performed. Cluster **1** was regenerated in moderate yield, indicating that the intermediate is primarily a deprotonated anion. Thus, K-Selectride is mainly functioning as a source of basic rather than nucleophilic hydride. A very small amount (< 1 mg from 20 mg of **1**) of another cluster product was obtained as two isomers in the ratio of 2:1, with ^1H NMR data indicating the presence of three hydrido ligands and regeneration of the aromatic ring. We believe that this product involves nucleophilic hydride attack on the co-ordinated $^-OC_6H_3OMe\text{-}4$, affording a $^-OC_6H_4OMe\text{-}4$ ligand, and subsequent protonation at the cluster core, and are attempting to obtain sufficient material to confirm this.

The reaction between **1** and K-Selectride in tetrahydrofuran, followed by auration with chloro(triphenylphosphine)gold(I) afforded a complex mixture of products from which the known (hydrido)carbonyl cluster $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ has been identified along with a new mixed-metal raft cluster $[AuRu_6(\mu_3\text{-}H)(\mu\text{-}O{:}\mu\text{-}C{:}\eta^6\text{-}OC_6H_3OMe\text{-}4)(CO)_{16}(PPh_3)]$ **2**, obtained in



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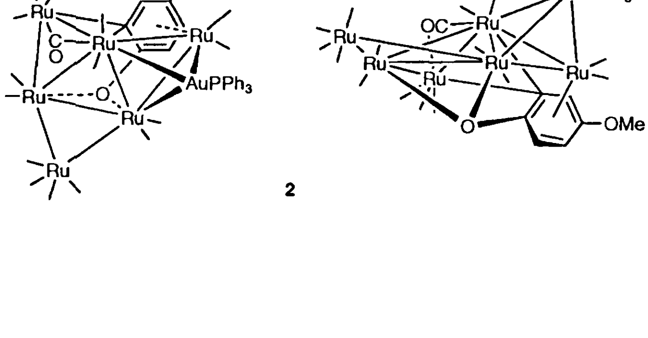

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

24% yield. The heptanuclear cluster **2** was characterized by the usual spectroscopic methods. The IR spectrum shows a band at 1870 cm^{-1} indicative of a bridging carbonyl, as well as absorptions due to the terminal carbonyl ligands. The ^{1}H NMR spectrum contains the expected signals due to the phosphine group (δ 7.67–7.60), and the aryl (δ 6.88–3.35) and methoxy (δ 3.66) protons of the $^{-}OC_6H_3OMe$-4 ligand. A singlet resonance at δ −23.1 can be assigned to a face-capping metal-bound hydride, on the basis of similar assignments in the case of the structurally-characterized phosphite-substituted $^{-}OC_6H_4$ analogue $[Ru_6(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}O{:}\mu\text{-}C{:}\eta^6\text{-}OC_6H_4)(CO)_{15}\{P(OMe)_3\}]$.[6] In contrast to that of **1**, the ^{1}H NMR spectrum of **2** shows the presence of only one isomer. The ^{13}C NMR spectrum contains sixteen signals due to the co-ordinated carbonyl ligands between δ 208 and 180, and resonances assigned to the carbons of the phenyl and $^{-}OC_6H_3$-OMe-4 ligands. Cluster **2** is thus formally related to its precursor **1** by replacement of H by $Au(PPh_3)$. X-Ray structural studies of **1** and **2** have been carried out to ascertain whether isolobal replacement corresponds to isostructural replacement, and are described below.

X-Ray Structural Study of $[Ru_6(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}O{:}\mu\text{-}C{:}\eta^6\text{-}OC_6H_3OMe\text{-}4)(CO)_{16}]$ **1**.—The solid-state structure of **1** is shown in Fig. 1; crystallographic data are collected in Table 1, atomic coordinates are listed in Table 2, and selected bond lengths (Table 4) and cluster core bond angles (Table 5) are also given. The six metals are arranged in a raft configuration, a geometry reported in several complexes recently including three ruthenium examples.[4,6–8] The co-ordination geometry is completed by fifteen terminal and one edge-bridging carbonyl ligands, an edge-bridging and a face-capping hydrido ligands, and an edge-bridging $^{-}OC_6H_3OMe$-4 group metallated at the 2-position and η^6-bound to a further ruthenium. The peripheral metal–metal distances vary between 2.764(1) and 3.085(1) Å, with the longest edge bridged by a hydrido ligand located in the refinement. The transannular Ru–Ru distances (av. 3.02 Å) are longer than the peripheral ones (av. 2.89 Å); a hydrido ligand (also located) face caps the central triangle. Terminal carbonyl ligand geometries [Ru–CO 1.821(9)–1.952(9) (av. 1.89); RuC–O 1.12(1)–1.17(1) (av. 1.14 Å): Ru–C–O 175.2(8)–179.8(8)°] are not unusual, with the longest Ru–CO linkages associated with Ru(6). The edge-bridging carbonyl is somewhat unsymmetrical, with Ru(2)–C(43) 1.98(1) and Ru(4)–C(43) 2.176(8) Å.

Table 1 Summary of crystallographic data for $[Ru_6(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}O{:}\mu\text{-}C{:}\eta^6\text{-}OC_6H_3OMe\text{-}4)(CO)_{16}]$ **1** and $[AuRu_6(\mu_3\text{-}H)(\mu\text{-}O{:}\mu\text{-}C{:}\eta^6\text{-}OC_6H_3OMe\text{-}4)(CO)_{16}(PPh_3)]$ **2**

Compound	1	2
Formula	$C_{23}H_8O_{18}Ru_6$	$C_{41}H_{22}AuO_{18}PRu_6$
M	1178.7	1637
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	11.122(4)	24.305(10)
b/Å	16.247(6)	11.558(3)
c/Å	17.562(5)	18.353(6)
β/°	91.71(3)	111.49(3)
U/Å^3	3172(2)	4797(3)
Z	4	4
D_c/g cm^{-3}	2.47	2.27
μ_{Mo}/cm^{-1}	28.6	49.9
Specimen/mm	0.26 × 0.13 × 0.12	0.08 × 0.26 × 0.10
$A^*_{min,max}$	1.39, 2.14	1.40, 1.80
F(000)	2216	3080
θ_{max}/°	27.5	25
N	7271	8438
N_o	4775	2641
R	0.037	0.071
R'	0.037	0.065

The $^{-}OC_6H_3OMe$-4 ligand co-ordinates in a similar fashion to the phenoxo ligand in the previously reported rafts $[Ru_6(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}O{:}\mu\text{-}C{:}\eta^6\text{-}OC_6H_4)(CO)_{16}]$[4,6,8] and $[Ru_6(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}O{:}\mu\text{-}C{:}\eta^6\text{-}OC_6H_4)(CO)_{15}\{P(OMe)_3\}]$.[6] The *O* atom symmetrically bridges Ru(3) and Ru(5) [Ru(3)–O(81) 2.159(5), Ru(5)–O(81) 2.132(5) Å]. The metallated 2-carbon of the aryl is unsymmetrically disposed with Ru(1)–C(86) 2.391(7), Ru(2)–C(86) 2.324(7) and Ru(4)–C(86) 2.215(7) Å. The η^6-co-ordination of the $^{-}OC_6H_3OMe$-4 ligand to Ru(1) is also unsymmetrical; while distances to the other five carbons fall in the range 2.271(8)–2.338(7) (av. 2.30 Å), Ru(1)–C(86) is exceptionally long [2.391(7) Å]. As the other bonding interactions of the aryl moiety hold it in the cleft defined by Ru(1)–Ru(5), speculations as to the degree of bonding between Ru(1) and C(86), and to whether the arene is η^6- or η^5-bound are probably not warranted.

X-Ray Structural Study of $[AuRu_6(\mu_3\text{-}H)(\mu\text{-}O{:}\mu\text{-}C{:}\eta^6\text{-}OC_6H_3OMe\text{-}4)(CO)_{16}(PPh_3)]$ **2**.—The solid-state structure of **2** is shown in Fig. 2, crystallographic data are collected in Table 1, atomic coordinates are listed in Table 3, and selected bond lengths (Table 4) and cluster core bond angles (Table 5) are also given. The structural study confirms the auration of the

(a)

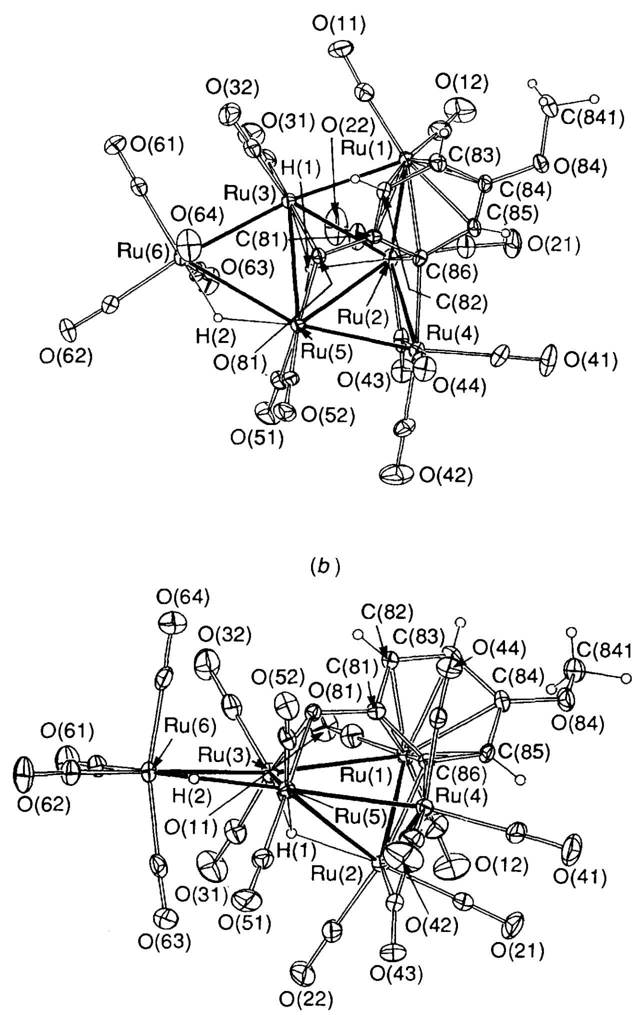

Fig. 1 Molecular structure and crystallographic numbering scheme for $[Ru_6(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}O{:}\mu\text{-}C{:}\eta^6\text{-}OC_6H_3OMe\text{-}4)(CO)_{16}]$ **1**; 20% thermal ellipsoids are shown for the non-hydrogen atoms. Hydrogen atoms have arbitrary radii of 0.1 Å. Projections are shown normal (*a*) and oblique (*b*) to the Ru_5 plane defined by Ru(1), Ru(3), Ru(4), Ru(5) and Ru(6) [χ^2 41 820; δ Ru(1,3,4,5,6) −0.099(1), 0.168(1), 0.065(1), −0.093(1), −0.040(1) Å; δ Ru(2) 1.727(1) Å]

Table 2 Atomic coordinates for [$Ru_6(\mu_3$-H)(μ-H)(μ-*O*:μ-*C*:η^6-OC_6H_3OMe-4)$(CO)_{16}$] **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.646 46(5)	0.637 88(4)	0.898 29(4)	C(52)	0.602 0(6)	0.521 9(5)	0.578 2(4)
Ru(2)	0.627 62(5)	0.740 12(4)	0.754 76(4)	O(52)	0.635 2(5)	0.471 7(4)	0.538 1(3)
Ru(3)	0.443 15(5)	0.611 81(4)	0.794 87(4)	C(61)	0.151 9(7)	0.561 2(5)	0.750 7(5)
Ru(4)	0.780 97(5)	0.653 76(4)	0.659 37(4)	O(61)	0.077 7(5)	0.559 9(4)	0.793 2(4)
Ru(5)	0.545 17(5)	0.601 47(4)	0.642 72(3)	C(62)	0.182 5(7)	0.528 5(5)	0.591 2(5)
Ru(6)	0.281 61(5)	0.561 77(4)	0.678 75(4)	O(62)	0.121 9(6)	0.511 0(5)	0.541 3(4)
C(11)	0.523 7(8)	0.619 5(5)	0.965 9(5)	C(63)	0.269 5(7)	0.679 4(6)	0.657 3(5)
O(11)	0.452 4(6)	0.611 3(5)	1.011 5(4)	O(63)	0.266 3(5)	0.747 0(4)	0.644 1(4)
C(12)	0.647 1(9)	0.743 8(6)	0.939 9(5)	C(64)	0.337 1(7)	0.451 3(6)	0.702 6(5)
O(12)	0.645 5(7)	0.806 5(4)	0.969 1(5)	O(64)	0.371 9(7)	0.386 5(4)	0.713 9(5)
C(21)	0.739 9(7)	0.815 2(5)	0.796 6(5)	C(81)	0.666 7(6)	0.552 7(4)	0.792 9(4)
O(21)	0.810 8(6)	0.860 3(4)	0.817 5(4)	O(81)	0.575 0(4)	0.532 5(3)	0.744 8(3)
C(22)	0.507 5(8)	0.820 3(5)	0.759 8(6)	C(82)	0.679 9(7)	0.506 4(5)	0.860 4(5)
O(22)	0.434 5(6)	0.869 2(4)	0.759 1(6)	C(83)	0.765 6(7)	0.524 8(5)	0.918 5(5)
C(31)	0.336 0(8)	0.688 5(6)	0.831 6(5)	C(84)	0.844 5(6)	0.589 9(5)	0.906 7(5)
O(31)	0.267 2(6)	0.734 6(5)	0.850 9(4)	O(84)	0.936 5(4)	0.610 9(3)	0.955 4(3)
C(32)	0.371 5(7)	0.534 3(6)	0.853 1(5)	C(841)	0.925(1)	0.593 3(7)	1.034 1(6)
O(32)	0.325 4(6)	0.484 8(5)	0.890 4(4)	C(85)	0.827 5(7)	0.638 5(5)	0.841 3(5)
C(41)	0.928 3(7)	0.709 1(5)	0.683 7(6)	C(86)	0.743 5(6)	0.623 6(4)	0.779 4(4)
O(41)	1.014 8(6)	0.745 1(5)	0.695 9(5)	H(1)	0.500(6)	0.674(4)	0.712(4)
C(42)	0.798 5(8)	0.668 6(6)	0.552 9(6)	H(2)	0.393(6)	0.566(4)	0.619(4)
O(42)	0.808 1(8)	0.675 9(6)	0.489 3(5)	H(82)	0.630(5)	0.469(4)	0.866(3)
C(43)	0.687 6(7)	0.771 4(5)	0.654 0(6)	H(83)	0.773(6)	0.495(4)	0.962(4)
O(43)	0.685 2(5)	0.825 4(3)	0.610 4(4)	H(841a)	0.864(9)	0.618(6)	1.053(6)
C(44)	0.845 9(7)	0.542 6(5)	0.657 6(5)	H(841b)	0.933(6)	0.546(4)	1.041(4)
O(44)	0.890 4(6)	0.480 6(4)	0.654 8(4)	H(841c)	1.003(6)	0.620(4)	1.061(4)
C(51)	0.513 5(7)	0.667 5(5)	0.558 2(5)	H(85)	0.876(6)	0.679(4)	0.844(4)
O(51)	0.492 4(7)	0.707 1(4)	0.506 6(4)				

Table 3 Non-hydrogen atomic coordinates for [$AuRu_6(\mu_3$-H)(μ-*O*:μ-*C*:η^6-OC_6H_3OMe-4)$(CO)_{16}(PPh_3)$] **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au	0.789 94(8)	0.771 6(1)	0.843 37(9)	O(62)	0.645(1)	1.413(3)	0.886(2)
Ru(1)	0.673 7(1)	0.692 2(2)	0.797 5(2)	C(63)	0.751(2)	0.185(4)	0.885(3)
Ru(2)	0.717 8(1)	0.902 8(3)	0.719 3(2)	O(63)	0.799(1)	1.212(3)	0.880(2)
Ru(3)	0.703 9(1)	0.934 7(3)	0.877 7(2)	C(64)	0.608(2)	1.114(4)	0.901(2)
Ru(4)	0.607 8(1)	0.972 9(3)	0.610 5(2)	O(64)	0.561(1)	1.090(2)	0.895(2)
Ru(5)	0.644 7(2)	1.094 8(3)	0.751 2(2)	P	0.880 4(5)	0.690(1)	0.904 0(7)
Ru(6)	0.686 3(2)	1.161 8(3)	0.908 0(2)	C(111)	0.948(2)	0.777(5)	0.909(3)
C(11)	0.703(2)	0.671(3)	0.904(2)	C(112)	0.995(4)	0.700(7)	0.906(4)
O(11)	0.713(1)	0.645(2)	0.968(2)	C(113)	1.041(4)	0.781(9)	0.910(5)
C(12)	0.721(2)	0.575(5)	0.793(3)	C(114)	1.038(3)	0.893(7)	0.908(4)
O(12)	0.748(1)	0.490(3)	0.794(2)	C(115)	0.989(3)	0.966(5)	0.907(3)
C(21)	0.745(2)	0.787(4)	0.668(3)	C(116)	0.939(2)	0.887(5)	0.907(3)
O(21)	0.762(1)	0.723(3)	0.636(2)	C(121)	0.895(3)	0.655(5)	1.001(3)
C(22)	0.786(2)	0.971(4)	0.747(2)	C(122)	0.858(3)	0.586(6)	1.018(4)
O(22)	0.832(1)	1.021(3)	0.766(2)	C(123)	0.863(3)	0.545(6)	1.094(5)
C(31)	0.771(2)	0.945(3)	0.944(2)	C(124)	0.909(5)	0.597(9)	1.153(5)
O(31)	0.825(1)	0.956(3)	0.991(2)	C(125)	0.952(4)	0.658(8)	1.147(6)
C(32)	0.684(2)	0.911(3)	0.958(2)	C(126)	0.944(4)	0.680(6)	1.063(5)
O(32)	0.668(1)	0.885(2)	1.010(2)	C(131)	0.887(2)	0.560(4)	0.854(3)
C(41)	0.591(2)	0.884(4)	0.524(2)	C(132)	0.873(3)	0.576(5)	0.772(4)
O(41)	0.572(1)	0.819(2)	0.468(2)	C(133)	0.874(3)	0.468(7)	0.726(4)
C(42)	0.588(2)	1.113(4)	0.552(2)	C(134)	0.881(3)	0.366(6)	0.764(4)
O(42)	0.579(1)	1.200(3)	0.521(2)	C(135)	0.897(3)	0.355(6)	0.841(5)
C(43)	0.691(2)	1.004(4)	0.615(2)	C(136)	0.900(3)	0.448(6)	0.891(4)
O(43)	0.722(1)	1.055(2)	0.588(1)	C(81)	0.609(1)	0.850(3)	0.760(2)
C(44)	0.538(2)	0.974(3)	0.631(2)	O(81)	0.614 2(9)	0.948(2)	0.797(1)
O(44)	0.492(1)	0.972(2)	0.638(1)	C(82)	0.583(1)	0.756(3)	0.792(2)
C(51)	0.679(2)	1.205(4)	0.716(2)	C(83)	0.583(2)	0.640(3)	0.767(2)
O(51)	0.702(1)	1.284(3)	0.697(2)	C(84)	0.591(2)	0.628(3)	0.698(2)
C(52)	0.580(2)	1.184(4)	0.731(2)	O(84)	0.579(1)	0.517(2)	0.665(2)
O(52)	0.539(1)	1.244(3)	0.713(2)	C(841)	0.586(2)	0.491(4)	0.598(3)
C(61)	0.724(2)	1.161(4)	1.013(3)	C(85)	0.619(2)	0.708(3)	0.668(2)
O(61)	0.753(1)	1.166(3)	1.083(2)	C(86)	0.627(1)	0.830(3)	0.695(2)
C(62)	0.661(2)	1.324(5)	0.891(3)				

hexaruthenium raft. Due to the weak and limited data, a consequence of small crystal size, errors associated with the lighter atom bond length and angle data are less precise than in **1**. The hydrido ligand was not located; its positioning is reliant on less direct (crystallographic and spectroscopic) inferences. The hexaruthenium raft core of **2** is similar to that of the precursor **1**; substantial bond length differences [Ru(1)–Ru(2) 3.203(5) **2** *cf.* 3.021(1) Å **1**, Ru(1)–Ru(3) 3.127(4) **2** *cf.* 2.889(1) Å

1, Ru(5)–Ru(6) 2.789(4) **2** *cf.* 3.085(1) Å **1**] are associated with the μ_3-AuPPh$_3$ group [capping the Ru(1)Ru(2)Ru(3) face] and the loss of the edge-bridging hydrido ligand on Ru(5)–Ru(6). The Au–Ru interactions are unusually unsymmetrical [Au–Ru(1) 2.792(4), Au–Ru(2) 2.764(3), Au–Ru(3) 3.048(4) Å]; in [AuRu$_6$C(CO)$_{15}$(NO)(PPh$_3$)], the Au(PPh$_3$) unit also adopts this uncommon asymmetrical bonding mode with two short Au–Ru distances (mean 2.782 Å) and one long Au–Ru separation (3.19 Å).[9,10] Metal–ligand and intraligand distances are unexceptional, with detailed discussion precluded by the relative imprecision. Noteworthy is Au–C(12) [2.78(6) Å]; such short contacts often occur between coinage metals and

Table 4 Selected bond lengths (Å) and angles (°) for [Ru$_6$(μ_3-H)(μ-H)(μ-*O*:μ-*C*:η^6-OC$_6$H$_3$OMe-4)(CO)$_{16}$] **1**, [AuRu$_6$(μ_3-H)(μ-*O*:μ-*C*:η^6-OC$_6$H$_3$OMe-4)(CO)$_{16}$(PPh$_3$)] **2**, [Ru$_6$(μ_3-H)(μ-H)(μ-*O*:μ-*C*:η^6-OC$_6$H$_4$)(CO)$_{16}$] **3** and [Ru$_6$(μ_3-H)(μ-H)(μ-*O*:μ-*C*:η^6-OC$_6$H$_4$)(CO)$_{15}${P(OMe)$_3$}] **4**

Compound	1	2	3[a]	4[b]
Ru(1)–Ru(2)	3.021(1)	3.203(5)	3.050(1)	3.042(1)
Ru(1)–Ru(3)	2.889(1)	3.127(4)	2.857(1)	2.876(1)
Ru(2)–Ru(3)	3.023(1)	3.068(5)	2.994(1)	3.041(1)
Ru(2)–Ru(4)	2.803(1)	2.808(4)	2.813(1)	2.827(1)
Ru(2)–Ru(5)	3.111(1)	3.030(5)	3.107(1)	3.134(1)
Ru(3)–Ru(5)	2.939(1)	2.905(4)	2.953(1)	2.952(1)
Ru(3)–Ru(6)	2.798(1)	2.749(5)	2.801(1)	2.759(1)
Ru(4)–Ru(5)	2.764(1)	2.786(4)	2.766(1)	3.016(1)
Ru(5)–Ru(6)	3.085(1)	2.789(4)	3.081(1)	2.788(1)
Au–Ru(1)	—	2.792(4)	—	—
Au–Ru(2)	—	2.764(3)	—	—
Au–Ru(3)	—	3.048(4)	—	—
Au–P	—	2.27(1)	—	—
Ru(1)–C(81)	2.327(7)	2.35(3)	2.322(3)	2.329(4)
Ru(1)–C(82)	2.271(8)	2.28(4)	2.282(4)	2.260(4)
Ru(1)–C(83)	2.287(8)	2.16(4)	2.269(4)	2.278(6)
Ru(1)–C(84)	2.338(7)	2.29(3)	2.275(3)	2.299(6)
Ru(1)–C(85)	2.275(8)	2.26(3)	2.286(3)	2.299(4)
Ru(1)–C(86)	2.391(7)	2.41(3)	2.410(3)	2.448(4)
Ru(2)–C(86)	2.324(7)	2.24(3)	2.347(3)	2.362(4)
Ru(4)–C(86)	2.215(7)	2.19(3)	2.214(3)	2.187(4)
Ru(3)–O(81)	2.159(5)	2.15(2)	2.173(2)	2.182(3)
Ru(5)–O(81)	2.132(5)	2.14(2)	2.131(2)	2.143(2)
C(81)–O(81)	1.345(8)	1.31(4)	1.343(3)	1.338(4)
Ru(2)–H(1)	1.92(7)	—	1.85(4)	1.94(5)
Ru(3)–H(1)	1.90(7)	—	1.99(4)	1.91(5)
Ru(5)–H(1)	1.77(7)	—	1.92(4)	1.92(5)
Ru(5)–H(2)	1.82(7)	—	1.81(5)	1.84(5)
Ru(6,*4*)–H(2)	1.65(7)	—	1.77(6)	*1.65(5)*

[a] Ref. 4; atoms renumbered to correspond with current labelling. [b] Ref. 5.

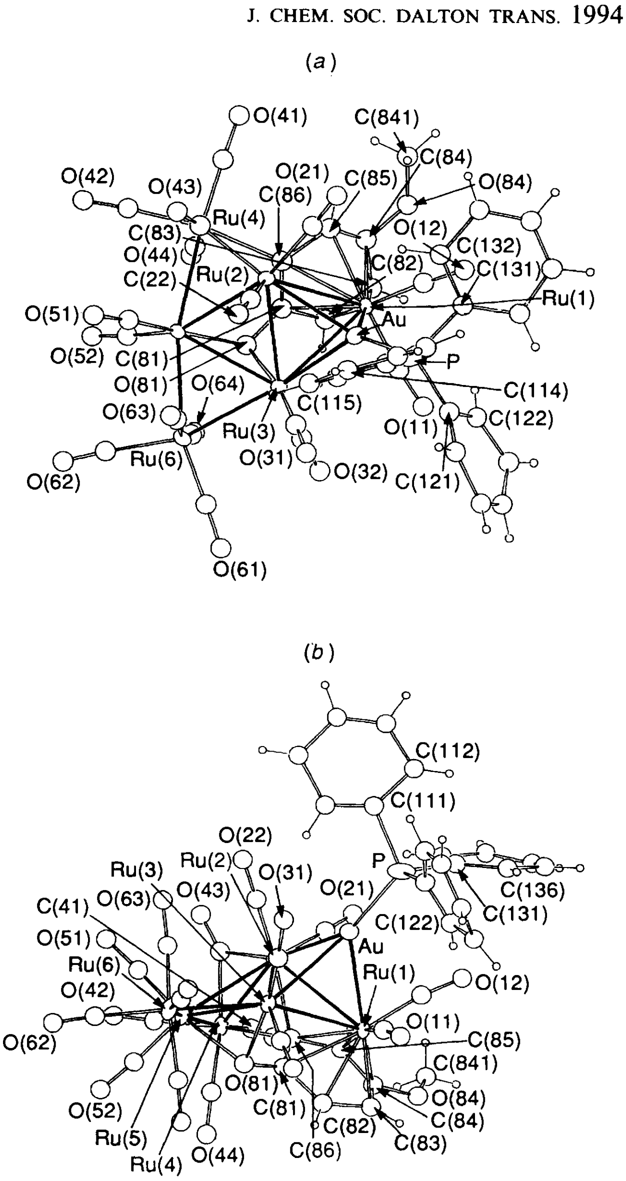

Fig. 2 Molecular structure and crystallographic numbering scheme for [AuRu$_6$(μ_3-H)(μ-*O*:μ-*C*:η^6-OC$_6$H$_3$OMe-4)(CO)$_{16}$(PPh$_3$)] **2**. Projections are shown normal (*a*) and oblique (*b*) to the Ru$_5$ plane defined by Ru(1), Ru(3), Ru(4), Ru(5) and Ru(6). [χ^2 5944; δ Ru(1,3,4,5,6) −0.122(4), 0.248(4), 0.038(5), −0.028(4), −0.166(5) Å; δ Ru(2), Au 1.776(4), 2.416(3) Å]

Table 5 Metal core bond angles (°) for [Ru$_6$(μ_3-H)(μ-H)(μ-*O*:μ-*C*:η^6-OC$_6$H$_3$OMe-4)(CO)$_{16}$] **1** and [AuRu$_6$(μ_3-H)(μ-*O*:μ-*C*:η^6-OC$_6$H$_3$OMe-4)(CO)$_{16}$(PPh$_3$)] **2**

Compound	1	2	Compound	1	2
Ru(2)–Ru(1)–Ru(3)	61.48(3)	58.0(1)	Ru(3)–Ru(5)–Ru(4)	106.09(3)	108.4(1)
Ru(1)–Ru(2)–Ru(3)	57.11(2)	59.8(1)	Ru(3)–Ru(5)–Ru(6)	55.29(2)	57.7(1)
Ru(1)–Ru(2)–Ru(4)	101.26(3)	98.6(1)	Ru(4)–Ru(5)–Ru(6)	161.24(3)	165.7(2)
Ru(1)–Ru(2)–Ru(5)	98.13(3)	98.9(1)	Ru(3)–Ru(6)–Ru(5)	59.69(3)	63.3(1)
Ru(3)–Ru(2)–Ru(4)	102.91(3)	103.5(2)	Ru(1)–Au(1)–Ru(2)	—	70.4(1)
Ru(3)–Ru(2)–Ru(5)	57.23(3)	56.9(1)	Ru(1)–Au(1)–Ru(3)	—	64.6(1)
Ru(4)–Ru(2)–Ru(5)	55.43(3)	56.9(1)	Ru(2)–Au(1)–Ru(3)	—	63.5(1)
Ru(1)–Ru(3)–Ru(2)	61.41(3)	62.3(1)	Au(1)–Ru(1)–Ru(2)	—	54.39(9)
Ru(1)–Ru(3)–Ru(5)	105.30(3)	103.4(1)	Au(1)–Ru(1)–Ru(3)	—	61.7(1)
Ru(1)–Ru(3)–Ru(6)	166.99(3)	157.6(1)	Au(1)–Ru(2)–Ru(1)	—	55.21(9)
Ru(2)–Ru(3)–Ru(5)	62.90(2)	60.9(1)	Au(1)–Ru(2)–Ru(3)	—	62.76(9)
Ru(2)–Ru(3)–Ru(6)	117.13(2)	112.7(1)	Au(1)–Ru(2)–Ru(4)	—	153.7(2)
Ru(5)–Ru(3)–Ru(6)	65.02(3)	59.0(1)	Au(1)–Ru(2)–Ru(5)	—	118.9(1)
Ru(2)–Ru(4)–Ru(5)	67.95(3)	65.6(1)	Au(1)–Ru(3)–Ru(1)	—	53.75(9)
Ru(2)–Ru(5)–Ru(3)	59.87(2)	62.2(1)	Au(1)–Ru(3)–Ru(2)	—	53.73(9)
Ru(2)–Ru(5)–Ru(4)	56.62(2)	57.6(1)	Au(1)–Ru(3)–Ru(5)	—	113.9(1)
Ru(2)–Ru(5)–Ru(6)	106.59(3)	112.7(1)	Au(1)–Ru(3)–Ru(6)	—	143.3(2)

essentially linear carbonyl ligands which are bonded to adjacent metals. It is not clear whether the short M···C contacts represent some degree of long-range interaction or result from steric effects in the solid.[11]

The structural studies emphasize the caution that must be exercised in applying the isolobal analogy; replacement of H by $Au(PPh_3)$ has occurred at a different site on the raft core, although in almost all compounds where structural comparisons are possible, the $Au(PR_3)$ fragment occupies a similar position to that of the isolobal hydrido ligand in the related hydrido metal cluster.[12] We believe that the remaining hydride caps the central raft triangle as in the precursor, there being no obvious bond lengthening elsewhere in the cluster to suggest a different site; spectroscopic data are consistent with this assignment (see above).

A number of raft clusters of the iron group have been prepared and structurally characterized, namely $[Os_6(CO)_{17}\{P(OMe)_3\}_4]$,[13] $[Os_6(\mu_3-O)(\mu_3-CO)(CO)_{18}]$,[14] $[Os_6\{C{=}C(H)Ph\}(CO)_{20}]$,[15] $[Os_6(\mu_3-S)_3(CO)_{15}]$[16] and $[Ru_6(\mu_3-H)(\mu_3-S)_3(CO)_{15}]^-$,[7] together with the aforementioned examples. Complex **2** is thus the first metallated derivative of a homometallic raft, although some heterometallic raft clusters are known {*e.g.* $[Fe_3Pt_3(CO)_{15}]^{-}$[17] and $[\{Os_3(CO)_{11}Hg\}_3]$[18]}.

All parent hexaruthenium raft clusters with co-ordinated phenol-derived ligands exist as mixtures of isomers: **1** (2:1), **3** (9:1) and $[Ru_6(\mu_3-H)(\mu-H)(\mu-O{:}\mu-C{:}\eta^6-OC_{10}H_7)(CO)_{16}]$ (3:1).[1] The nature of this isomerism has been the subject of speculation.[6] Replacement of CO by $P(OMe)_3$ in **3**,[6] or replacement of H by $Au(PPh_3)$ (this work) afford just one product. Using NMR arguments, Bhaduri *et al.*[6] have assigned the parent raft isomerism to differing edge-bridging hydrido ligand sites. The substitution chemistry tends to support this; replacement of CO by $P(OMe)_3$ affords an electron-rich ruthenium to which the hydride preferentially ligates, and replacement of μ-H by $Au(PPh_3)$ removes the isomerism also.

Experimental

The cluster $[Ru_6(\mu_3-H)(\mu-H)(\mu-O{:}\mu-C{:}\eta^6-OC_6H_3OMe-4)(CO)_{16}]$ was prepared as reported previously.[1] The reagents K-Selectride and $[AuCl(PPh_3)]$ were obtained from Aldrich and used as received. Tetrahydrofuran was dried over sodium wire and distilled from sodium-benzophenone. CH_2Cl_2 was dried and distilled over CaH_2. Light petroleum refers to that fraction boiling in the range 60–70 °C. The reaction was carried out using standard Schlenk techniques[19] under an atmosphere of dry nitrogen, although subsequent work-up was carried out without any precautions to exclude air. Column chromatography utilised Kieselgel 60 (70–230 mesh ASTM) silica from Merck. Thin layer chromatography was carried out on glass plates (20 × 20 cm) coated with Merck GF_{254} silica gel (0.5 mm). IR spectra were recorded using a Perkin Elmer model 1725 Fourier transform spectrophotometer with CaF_2 optics. NMR spectra were recorded on a Bruker AM300 spectrometer, the ^1H spectra at 300.13 MHz, the ^{13}C at 75.47 MHz. Elemental miroanalyses were by the Microanalytical Service in the Department of Chemistry, University of Queensland.

Reactions of $[Ru_6(\mu_3-H)(\mu-H)(\mu-O{:}\mu-C{:}\eta^6-OC_6H_3OMe-4)(CO)_{16}]$.—*With* H_2. Hydrogen gas was bubbled through a refluxing solution of $[Ru_6(\mu_3-H)(\mu-H)(\mu-O{:}\mu-C{:}\eta^6-OC_6H_3OMe-4)(CO)_{16}]$ (50 mg, 0.042 mmol) in benzene (170 cm^3) for 16 h. The resulting red-brown solution was taken to dryness and a CH_2Cl_2 extract subjected to column chromatography. Elution with light petroleum gave an orange band identified as $[Ru_4(\mu-H)_4(CO)_{12}]$ by its IR spectrum (7 mg, 23%). Elution with CH_2Cl_2–light petroleum (1:1) followed by acetonitrile–CH_2Cl_2 (12:78) yielded several as yet unidentified brown bands.

With K-Selectride–H_3PO_4. K-Selectride (20 μl of a 1 mol dm^{-3} solution in thf) was added to a solution of $[Ru_6(\mu_3-H)(\mu-H)(\mu-O{:}\mu-C{:}\eta^6-OC_6H_3OMe-4)(CO)_{16}]$ (20 mg, 0.017 mmol) in thf (10 cm^3) at −63 °C. The solution was stirred for 15 min as it was allowed to return to room temperature, at which stage a solution IR spectrum indicated no starting material remained. The solvent was removed *in vacuo* and the mixture taken up in freshly distilled CH_2Cl_2 (15 cm^3). Phosphoric acid (4 drops) was added dropwise over 30 min to the stirred solution until no starting material was evident in the IR spectrum. The mixture was taken to dryness and subjected to TLC. Elution with CH_2Cl_2–light petroleum (3:7) yielded four bands. The first band was identified as $[Ru_4(\mu-H)_4(CO)_{12}]$ by IR and NMR spectroscopy (1 mg, 7%). Band 2 was similarly identified as $[Ru_4(\mu-H)_2(CO)_{13}]$ (1 mg, 4%). Band 3 was obtained as a red powder from CH_2Cl_2–hexane (< 1 mg); ν_{max}(CO) 2115w, 2102w, 2081m, 2073m, 2056w, 2046s, 2044 (sh), 2037m, 2029s, 2023m, 2016m, 1994w, 1987w, 1982w, 1976w, 1972w, 1963w and 1810wm cm^{-1} (CH_2Cl_2); $\delta_H(CDCl_3)$ 7.69 (m), 7.51 (m), 4.21 (m), 3.27 (s) (phenoxy ligand), Ru–H signals in two sets in the ratio of 2:1 at δ −13.35, −15.70, −21.21 and −11.61, −16.76, −21.04. Band 4 was identified as regenerated starting material **1** (8 mg, 40%).

With K-Selectride–$[AuCl(PPh_3)]$. A solution of $[Ru_6(\mu_3-H)(\mu-H)(\mu-O{:}\mu-C{:}\eta^6-OC_6H_3OMe-4)(CO)_{16}]$ (50 mg, 0.0424 mmol) in thf (10 cm^3) was cooled to −63 °C and K-Selectride (45 μl of a 1 mol dm^{-3} solution in thf) was introduced *via* syringe. The solution was stirred for 20 min, at which stage no starting material was evident by IR spectroscopy. A mixture of $[AuCl(PPh_3)]$ (21 mg, 0.0424 mmol) and $AgBF_4$ (12 mg, 0.616 mmol) was stirred in thf (10 cm^3) for 15 min and added through a Schlenk filter to the dark red reaction mixture. The solution was allowed to come to room temperature and stirred for 16 h. Subsequent purification by TLC [CH_2Cl_2–light petroleum (1:4)] yielded several bands. The first yellow band was identified by its IR and NMR spectra as $[Ru_4(\mu-H)_4(CO)_{12}]$ (2 mg, 6%). Band 6 was similarly identified as unreacted starting material (**1**; 8 mg, 16%). Band 5 was identified by its IR spectrum as the same trihydride product obtained above (band 3 above, < 1 mg). The dark red band 7 was crystallized from CH_2Cl_2–hexane to give red-black crystals of $[AuRu_6(\mu_3-H)(\mu-O{:}\mu-C{:}\eta^6-OC_6H_3OMe-4)(CO)_{16}(PPh_3)]\cdot CH_2Cl_2$ **2** (17 mg, 21%) (Found: C, 29.15; H, 1.25. $C_{41}H_{22}AuO_{18}PRu_6\cdot CH_2Cl_2$ requires C, 29.30; H, 1.40%); ν_{max}(CO) 2138w, 2085m, 2051s, 2027s, 2015s, 1991m, 1930w and 1870w cm^{-1} (CH_2Cl_2); $\delta_H(CDCl_3)$ 7.67–7.60 (15 H, m, phosphine), 6.88 [1 H, dd, ^3J(HH) 7, ^4J(HH) 3, H^3], 5.28 (2 H, s, CH_2Cl_2), 3.96 [1 H, d, ^3J(HH) 7, H^2], 3.66 (3 H, s, OMe), 3.35 [1 H, d, ^4J(HH) 3, H^5] and −23.1 (1 H, s, Ru–H); $\delta_C(CDCl_3)$ 207.1, 206.5, 206.2, 206.1, 205.8, 205.1, 204.1, 203.8, 200.9, 198.6, 197.6, 192.2, 192.0, 188.3, 186.5, 183.3 (CO); 134.0 [d, *J*(CP) 14, *o*-C], 131.8 [d, *J*(CP) 49, *ipso*-C], 131.3 (s, *p*-C), 129.1 [d, *J*(CP) 11 Hz, *m*-C] (phosphine); 136.6 (C^6), 136.1 (C^1), 120.2 (C^4), 99.8 (C^3), 78.7 (C^2) and 75.1 (C^5) (phenol).

Structure Determination.—Single crystals of clusters **1** and **2** suitable for the X-ray work were grown from CH_2Cl_2–hexane at ≈ −20 °C. Unique diffractometer data sets (2θ–θ scan mode; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å) were measured at ≈295 K, yielding *N* independent reflections, N_o of these with $I > 3\sigma(I)$ being considered observed and used in the full-matrix least-squares refinements after absorption corrections [Gaussian (**1**), analytical (**2**)]. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x,y,z,U_{iso})_H$ for the ligand hydrogen atoms were constrained at estimated values, while those for the core hydrogen atoms were refined in **1**. Conventional residuals on $|F|$, *R* and *R'* are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Neutral atom complex scattering factors were employed; computation used the XTAL 3.2 program system implemented by S. R. Hall.[20] Pertinent results are given in the Figures and Tables.

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

Abormal features/variations in procedure. For **1** all hydrogen atoms were refined in (x,y,z,U_{iso}). For **2** the crystal decomposes by *ca.* 20% during data collection, as evidenced by deterioration in the periodic standard reflections; data were scaled accordingly in compensation. In consequence of weak data, anisotropic thermal parameters were used only for Ru, Au and P. The hydrido ligand was not located.

Acknowledgements

We thank the Australian Research Council for support of this work and Johnson-Matthey Technology Centre for the loan of ruthenium salts. M. P. C. holds a University of New England Postgraduate Research Scholarship. T. P. J. was the recipient of a University of New England Vacation Research Scholarship.

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Received 7th September 1993; *Paper* 3/05351B