Isolation and *X*-ray Structure Determination of $H_2Ru_6(CO)_{16}(C_6H_4O)$, a Hydridoruthenium 'Raft' Cluster

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$H_2Ru_6(CO)_{16}(C_6H_4O)$ (**1**) has been isolated from the reaction of $Ru_3(CO)_{12}$ with phenol; *X*-ray analysis has shown (**1**) to possess a 'raft' type metal framework and a novel bonding mode of the aromatic ring.

$Ru_3(CO)_{12}$ is known to be an efficient precatalyst for hydrogen transfer from alcohols to suitable acceptors.[1] Since involvement of alkoxo clusters as catalytic intermediates is a possibility, we have studied the reaction of $Ru_3(CO)_{12}$ with phenol in an attempt to isolate such species and investigate their reactivity. The resultant phenoxo derivatives should be stable, since the β-hydride elimination leading to hydrido derivatives is impossible.[2] Here we report the *X*-ray structure and 500 MHz ^1H n.m.r. data on (**1**), one of the complexes isolated from this reaction. To our knowledge this is the first ruthenium cluster where the six metal atoms adopt a 'raft' configuration. Both *X*-ray and n.m.r. data indicate a novel interaction between the aromatic ring and the metal skeleton.

Reaction of $Ru_3(CO)_{12}$ with phenol in cyclohexane at 80 °C for 16 h leads to the formation of $H_4Ru_4(CO)_{12}$ (~20%), $H_2Ru_4(CO)_{13}$ (~20%), (**1**) (~40%), and some other carbonyl species yet to be characterised.†

In the ^1H n.m.r. spectrum of (**1**)† the chemical shifts of the

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† *Spectroscopic data* for (**1**), i.r. (cyclohexane): 2114(m), 2102(w), 2076(s), 2048(vs), 2026(s), 2018(s,sh), 2000(w), 1972(m), 1951(w), and 1813(m) cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ 6.93(t), 6.12(t), 4.26(d), 3.64(d); −11.79 and −21.86 (Ru–H). ^{13}C {^1H} N.m.r. ($CDCl_3$): 118.7, 110.73, 105.92, 99.39, 91.30, and 82.15.

^1H N.m.r. of the isomer in $CDCl_3$: δ 6.83 (t), 5.89(t), 4.03(d), 3.83(d), −12.85(s), and −22.02(s).

upfield protons (δ 4.26 and 3.64) are close to the region (δ 4.14 to 4.46) where signals of protons from face capping benzene rings have been observed.[3] Substantial differences in the electronic environments of the ring protons are indicated by the observed range of chemical shifts. The n.m.r. spectrum also indicates the presence of a small amount (<15%) of a second isomer. Weak but clear signals are associated with all the ring protons and the metal hydrides.[†] Variable temperature n.m.r. experiments (+50 to −50 °C) show little change in the relative concentrations of the two isomers, indicating that they are not in equilibrium. The two signals observed for the hydride ligands have a separation of ~10 p.p.m. and no exchange is observed up to +50 °C.

The molecular structure of (**1**) as determined by *X*-ray diffraction is shown in Figure 1.[‡] The six ruthenium atoms adopt a 'raft' configuration which has previously been observed in some osmium clusters and an Fe–Pt mixed cluster.[4,5,6] A ruthenium anionic cluster, $[\mathrm{HRu_6(O{=}CNMe_2)_2(CO)_{18}}]^-$ (**2**) with a cyclical array of six ruthenium atoms has been reported.[7] However, the absence of transannular Ru–Ru linkages in this complex rules out the description of the metal core as a 'raft'. The average metal–metal distances of the inner triangles in clusters $\mathrm{Os_6(CO)_{17}[P(OMe)_3]_4}$, (**1**), and (**2**) are 2.842(2), 3.018(2), and 3.227(2) Å, respectively.[5,7] Based on the reasonable assumption that '$\mathrm{OC_6H_4}$' and '$\mathrm{O{=}CNMe_2}$' moieties donate 10 and 5 valence electrons, the total number of valence electrons in the three clusters are 90, 92, and 96, respectively. In (**1**) the lengthening of the Ru–Ru distances of the inner triangle must be partly due to the presence of the triply bridging hydride, and occupancy of the low-lying antibonding molecular orbital shown to be present by Evans and Mingos in 90-electron 'raft' systems.[8] In (**1**) both the hydride positions are consistent with potential energy calculations.[9] The fused metal triangles in (**1**) show considerable puckering; the angles between the central Ru(2)–Ru(3)–Ru(5) plane and the Ru(2)–Ru(4)–Ru(5), Ru(3)–Ru(5)–Ru(6), and Ru(1)–Ru(2)–Ru(3) planes are 40, 36, and 42°, respectively.

While Ru(4) and, to a lesser extent, Ru(2) interact with C(2), the other five carbon atoms of the aromatic ring interact with Ru(1). The Ru(1) · · · C(2) distance is longer than those of all the other ring carbon atoms from Ru(1). It is also longer than the reported Ru–C distances between the two carbon atoms of a 'benzyne' moiety π-bonded to a ruthenium atom.[10] The Ru(1) · · · C(2) interaction is therefore considered to be negligible.

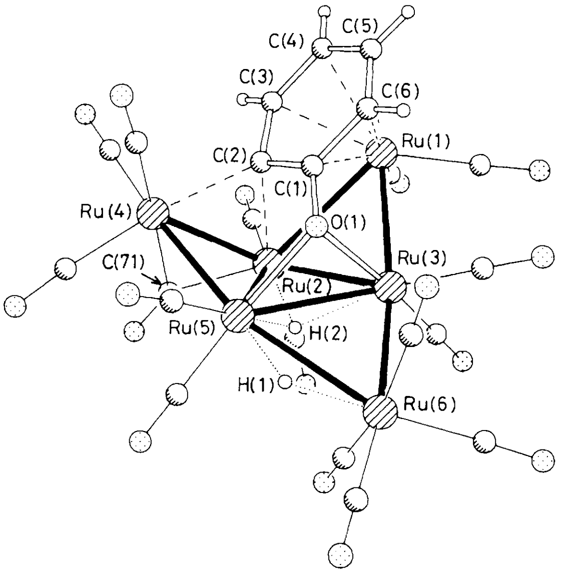

Figure 1. The molecule of (**1**) in the crystal (perspective view, radii arbitrary). Selected bond lengths (Å): Ru(1)–Ru(2) 3.050, Ru(1)–Ru(3) 2.857, Ru(2)–Ru(3) 2.994, Ru(2)–Ru(4) 2.813, Ru(2)–Ru(5) 3.107, Ru(3)–Ru(5) 2.953, Ru(3)–Ru(6) 2.801, Ru(4)–Ru(5), 2.766, Ru(5)–Ru(6) 3.081 (all ±0.001), Ru(1)–C(1) 2.322(3), Ru(1)–C(2) 2.410(3), Ru(1)–C(3) 2.286(3), Ru(1)–C(4) 2.275(3), Ru(1)–C(5) 2.269(4), Ru(1)–C(6) 2.282(4), Ru(2)–C(2) 2.347(3), Ru(2)–H(2) 1.85(4), Ru(3)–O(1) 2.173(2), Ru(3)–H(2) 1.99(4), Ru(4)–C(2) 2.214(3), Ru(5)–O(1) 2.131(2), Ru(5)–H(1) 1.81(5), Ru(5)–H(2) 1.92(4), Ru(6)–H(1) 1.77(6), Ru–carbonyl C 1.846—1.956 (terminal), Ru(2)–C(71) 1.991(3), Ru(4)–C(71) 2.130(3) (bridging), C(1)–O(1) 1.343(3), C–C 1.392—1.437.

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[‡] *Crystal data* for (**1**): $\mathrm{C_{22}H_6O_{17}Ru_6}$, M = 1148.6, monoclinic, space group $A2/a$ (non-standard setting of $C2/c$), a = 18.295(2), b = 9.066(1), c = 36.860(6) Å, β = 102.11(2)°, U = 5977 Å^3, Z = 8, D_x = 2.55 g cm^{-3}, $\lambda(\text{Mo-}K_\alpha)$ = 0.71069 Å, μ = 3.0 mm^{-1}, $F(000)$ = 4304. Data were collected on a Stoe-Siemens four-circle diffractometer using graphite-monochromated Mo-K_α radiation. The structure was solved by direct methods and refined to R 0.031, wR 0.036 for 8362 reflections having $F > 4\sigma(F)$ out of a total of 9890 unique reflections. All non-hydrogen atoms were refined anisotropically, organic H with riding model. The cluster hydrides were clearly visible in difference syntheses and were refined freely.

Full details of the structure determination have been deposited at the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, W. Germany. Any request for this material should quote a full literature citation and the reference number CSD 52678. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.