Synthesis and X-Ray Structural Studies on the Cluster Compounds [$RuRh_3(\mu_3$-$CO)_2(CO)_3(\eta$-$C_5Me_5)_3$] and [$RuRh_2(\mu$-$CO)(\mu_3$-$CO)(CO)_2(\eta^4$-$C_8H_{10})(\eta$-$C_5Me_5)_2$] †

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The compounds [$Ru(\eta^6$-$C_8H_{10})$(cod)] (C_8H_{10} = cyclo-octa-1,3,5-triene, cod = cyclo-octa-1,5-diene) and [$Rh(CO)_2(\eta$-$C_5Me_5)$] react in toluene at 60 °C to give the cluster compounds [$RuRh_3(\mu_3$-$CO)_2(CO)_3(\eta$-$C_5Me_5)_3$] (**1**) and [$RuRh_2(\mu$-$CO)(\mu_3$-$CO)(CO)_2(\eta^4$-$C_8H_{10})(\eta$-$C_5Me_5)_2$] (**2**). The structures of these compounds were established by single-crystal *X*-ray diffraction studies. Compound (**1**) has a distorted tetrahedral $RuRh_3$ metal atom core [Rh–Rh 2.684(1)—2.739(1), Ru–Rh 2.620(1)—2.715(1) Å]. The rhodium atoms are each ligated by an η-C_5Me_5 group, the ruthenium atom is terminally bonded to three carbonyl groups, while the remaining two CO ligands triply and asymmetrically bridge the Rh_3 face and one $RuRh_2$ face of the metal polyhedron. In compound (**2**) the C_8H_{10} ligand attached to the ruthenium is bicyclo[4.2.0]octa-2,4-diene. The molecule comprises a metal atom triangle [Ru–Rh 2.766(1) and 2.815(1), Rh–Rh 2.672(1) Å] and an η-C_5Me_5 group is co-ordinated to each rhodium atom. The four CO ligands show a remarkable variety of bonding modes. One carbonyl group attached to the ruthenium atom is essentially terminally bound to that centre [Ru–C–O 167.5(4)°], while a second carbonyl group attached to the ruthenium semi-bridges an edge of the metal triangle [Ru–C–O 158.1(4)°; Ru–CO 1.930(4), Rh $\cdots$ CO 2.412(5) Å]. The Rh–Rh vector is symmetrically bridged by another CO ligand [Rh–C–O 137.3(3) and 138.2(3)°, Rh–CO 1.989(3) and 2.000(4) Å]. The remaining carbonyl group asymmetrically bridges the face of the triangle [Ru–CO 2.247(4), Rh–CO 2.038(4) and 2.069(4) Å]. Spectroscopic studies (i.r. and n.m.r.) on (**1**) and (**2**) are reported. Both compounds show site exchange of CO groups in solution (^{13}C-{^1H} n.m.r.) but the process in (**1**) is limited to the $Ru(CO)_3$ group, with the dynamic behaviour persisting at −80 °C. With (**2**), at room temperature, all four CO ligands exchange, but at −80 °C separate signals for the μ-CO and μ_3-CO groups are seen, although only one resonance is observed for the two CO groups attached to the ruthenium atom. These and other data are discussed, and a mechanism proposed to account for the formation of (**1**) and (**2**).

By employing the complex [$Rh(CO)_2(\eta$-$C_5Me_5)$] as a precursor, we have recently prepared several cluster compounds having bonds between rhodium and other transition elements. Metal–ligand groups with an affinity for CO react with the mononuclear rhodium compound in such a manner that metal–metal bond formation is accompanied by transfer of CO from rhodium to another metal centre. Thus [$Rh(CO)_2(\eta$-$C_5Me_5)$] reacts with [$Pt(cod)_2$] (cod = cyclo-octa-1,5-diene) to give [$Rh_2Pt(\mu$-$CO)_2(CO)_2(\eta$-$C_5Me_5)_2$],[1] while the labile tetrahydrofuran (thf) complexes [$Mn(CO)_2$(thf)$(\eta$-$C_5H_5)$] and [$Cr(CO)_2$(thf)$(\eta$-$C_6H_6)$] yield the dimetal compounds [$MnRh(\mu$-$CO)_2(CO)_2(\eta$-$C_5H_5)(\eta$-$C_5Me_5)$] and [$CrRh(\mu$-$CO)_2(CO)_2(\eta$-$C_6H_6)(\eta$-$C_5Me_5)$], respectively.[2]

In order to extend the scope of these syntheses we have studied the reaction between [$Rh(CO)_2(\eta$-$C_5Me_5)$] and the zero-valent ruthenium complex [$Ru(\eta$-$C_8H_{10})$(cod)] which contains an η^6-ligated cyclo-octa-1,3,5-triene ligand.[3] It appears that only two mixed-metal complexes of rhodium and ruthenium have been previously reported, these being the tetra- and penta-nuclear clusters [$Ru_3Rh(\mu$-$H)(\mu_3$-$PPh)(CO)_{10}$-(PEt_3)] and [$Ru_3Rh_2(\mu_4$-$PPh)(CO)_{13}(PEt_3)$].[4] The known chemistry of [$Rh(CO)_2(\eta$-$C_5Me_5)$], and that of [$Ru(\eta^6$-$C_8H_{10})$(cod)] discussed below, made it probable that these species would combine to give compounds with Rh–Ru bonds, although the composition of the products would be difficult to predict.

† 1,2,3;1,2,4-Di-μ_3-carbonyl-4,4,4-tricarbonyl-1,2,3-tris(η-pentamethylcyclopentadienyl)trirhodiumruthenium(3 *Rh–Rh*)(3 *Rh–Ru*) and 3-(2′—5′-η-bicyclo[4.2.0]octa-2′,4′-diene)-1,2-μ-carbonyl-μ_3-carbonyl-3,3-dicarbonyl-1,2-bis(η-pentamethylcyclopentadienyl)-*triangulo*-dirhodiumruthenium.

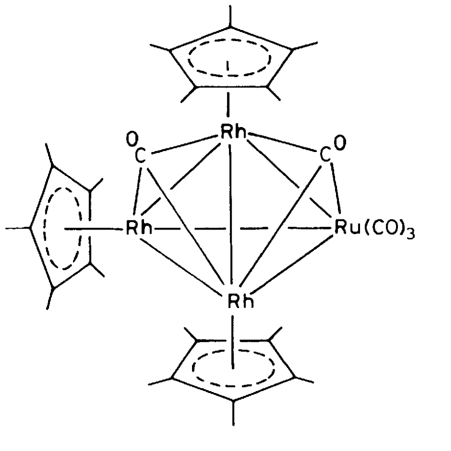
Supplementary data available (No. SUP 56085, 16 pp.): H-atom co-ordinates, thermal parameters, complete bond length and angle data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Results and Discussion

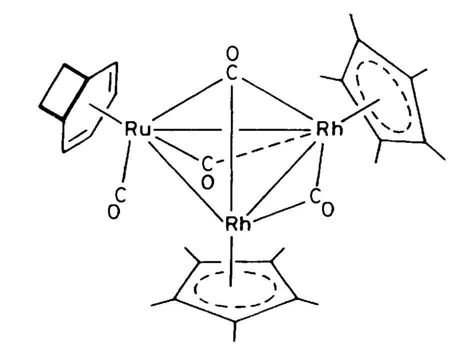
When a mixture of [$Ru(\eta^6$-$C_8H_{10})$(cod)] and [$Rh(CO)_2(\eta$-$C_5Me_5)$] is heated at *ca.* 60 °C in toluene, reaction occurs to give two crystalline products (**1**) and (**2**), which can be separated by column chromatography on alumina. The spectroscopic data for these compounds did not define their molecular structures, and hence single-crystal *X*-ray diffraction studies were carried out.

The molecular structure of the purple compound (**1**) is shown in Figure 1 and important distances and angles are given in Table 1. The results establish that (**1**) is a tetranuclear metal cluster with a $RuRh_3$ core structure, formally containing 60 cluster valence electrons (c.v.e.s). The metal atom core is a distorted tetrahedron, each rhodium is ligated by an η-C_5Me_5 group, with the ruthenium atom carrying three carbonyl ligands. The Rh_3 and Rh(2)Rh(3)Ru faces of the tetrahedron are asymmetrically capped by CO groups.

The molecule has an approximate, non-crystallographically imposed, plane of mirror symmetry defined by the metal atoms Rh(1) and Ru, and by the carbonyl groups C(1)O(1), C(4)O(4), and C(5)O(5). Not surprisingly, appropriately related pairs of internuclear distances and angles are almost equivalent. Thus



(1)



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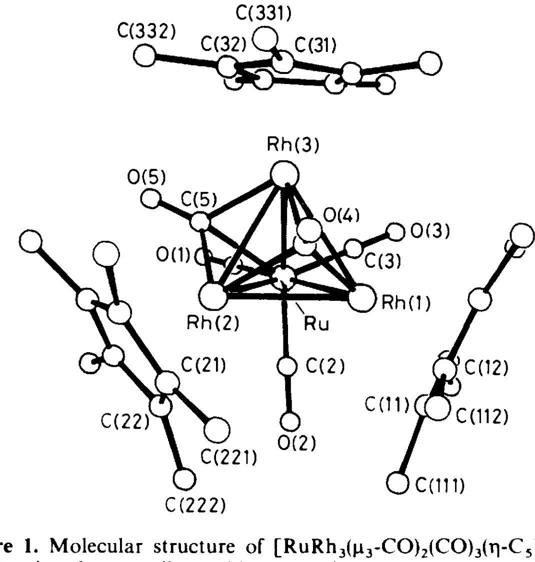


Figure 1. Molecular structure of $[RuRh_3(\mu_3\text{-}CO)_2(CO)_3(\eta\text{-}C_5Me_5)_3]$ (1), showing the crystallographic numbering

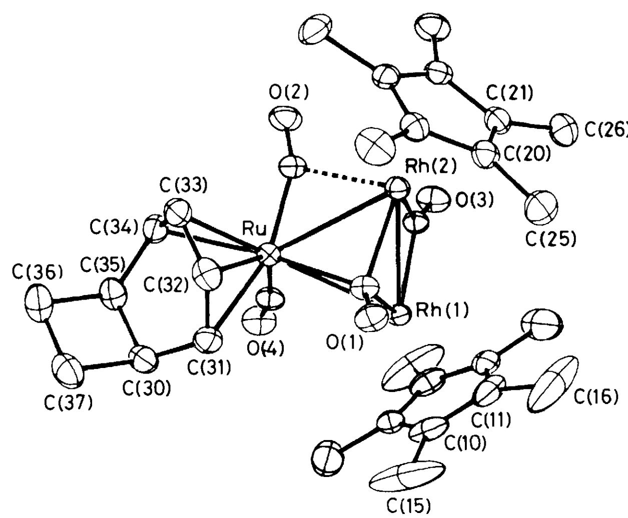


Figure 2. Molecular structure of $[RuRh_2(\mu\text{-}CO)(\mu_3\text{-}CO)(CO)_2(\eta^4\text{-}C_8H_{10})(\eta\text{-}C_5Me_5)_2]$ (2), showing the crystallographic numbering

the Rh(1)—Rh(2) [2.734(1) Å] and Rh(1)–Rh(3) [2.739(1) Å] separations are very similar, and both are longer than the remaining Rh(2)–Rh(3) distance [2.684(1) Å]. Comparable Rh–Rh distances are found in the compounds $[Ir_2Rh_2(\mu\text{-}CO)(\mu_3\text{-}CO)_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ [2.704(1) Å],[5] $[Rh_3(\mu\text{-}H)(\mu_3\text{-}CO)(\mu_3\text{-}C_2H_2)(\eta\text{-}C_5Me_5)_3][BF_4]$ [2.686(2) and 2.708(2) Å],[6] and $[Rh_3(\mu\text{-}H)_2(\mu\text{-}CO)(\mu_3\text{-}CO)(\eta\text{-}C_5Me_5)_3]$ [2.674(1) and 2.785(1) Å][6] which, like (**1**), are electronically saturated (*i.e.* 60 or 48 c.v.e.s). These Rh–Rh separations may be compared with the significantly shorter distances found in the 46-c.v.e. trirhodium compound $[Rh_3(\mu_3\text{-}CO)_2(\eta\text{-}C_5Me_5)_3]$ [2.553(1), 2.572(1), and 2.639(1) Å].[6] The Ru–Rh vectors in (**1**) [Ru–Rh(1) 2.620(1), Ru–Rh(2) 2.715(1), and Ru–Rh(3) 2.711(1) Å] are appreciably shorter than those in the compound $[Ru_3Rh_2(\mu_4\text{-}PPh)(CO)_{13}(PEt_3)]$ [2.930(1), 2.783(1), 2.862(1), and 2.758(1) Å].[4]

The μ_3-C(4)O(4) ligand has a relatively short Rh(1)–C(4) separation [1.971(5) Å], with two longer and almost equivalent connectivities to the remaining two rhodium atoms [Rh(2)–C(4) 2.176(5), Rh(3)–C(4) 2.147(5) Å]. In contrast, μ_3-C(5)O(5) has two short Rh–C(5) separations [Rh(2)–C(5) 2.028(5), Rh(3)–C(5) 2.053(5) Å] and a longer bond to the ruthenium atom [Ru–C(5) 2.214(5) Å]. The ruthenium atom is also ligated by three terminally bound CO groups, with only Ru–C(2)–O(2) [176.6(6)°] showing a slight deviation from linearity.

The spectroscopic data for (**1**) (Experimental section) were in accord with the structure established by *X*-ray diffraction. The i.r. spectrum showed bands at 1 690 and 1 667 cm^{-1}, characteristic of μ_3-CO groups, as well as three absorptions (2 008, 1 946, and 1 931 cm^{-1}) in the region expected for an $Ru(CO)_3$ group. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum, even when measured at −80 °C, showed one resonance (δ 197.9 p.p.m.) for the $Ru(CO)_3$ group, indicating that these three carbonyl groups undergo site exchange. However, both at room temperature and at −80 °C, there are two resonances for the μ_3-CO ligands. A quartet signal at δ 245.7 p.p.m. [*J*(RhC) 37 Hz] may be ascribed to C(4), and a triplet signal at δ 223.2 [*J*(RhC) 12 Hz] to C(5).

The molecular structure of the green compound (**2**) is shown in Figure 2, and selected internuclear distances and angles are listed in Table 2. The molecule contains a triangle of metal atoms. The ruthenium atom is co-ordinated by a bicyclo-[4.2.0]octa-2,4-diene ligand, evidently formed by isomerisation of the 1—6-η-cyclo-octa-1,3,5-triene group present in the precursor $[Ru(\eta\text{-}C_8H_{10})(cod)]$.[3] The isomerisation of cyclo-octa-1,3,5-triene to bicyclo[4.2.0]octa-2,4-diene in metal-complex chemistry is well established, and is particularly facile for ruthenium.[7] Both rhodium atoms carry $\eta\text{-}C_5Me_5$ groups.

Compound (**2**) shows a remarkable variation of CO bonding modes within a single structure. The C(4)O(4) group is essentially terminally bound to the ruthenium atom, but with some slight interaction with Rh(1) [Ru–C(4)–O(4) 167.5(4)°, Rh(1) ··· C(4) 2.750(5) Å]. The C(2)O(2) ligand can be described unambiguously as semi-bridging[8,9] [Ru–C(2)–O(2) 158.1(4)°; Ru–C(2) 1.930(4), Rh(2)–C(2) 2.412(5) Å], while C(3)–O(3)

Table 1. Selected internuclear distances (Å) and angles (°) for $[RuRh_3(\mu_3\text{-}CO)_2(CO)_3(\eta\text{-}C_5Me_5)_3]$ (**1**)*

Rh(1)–Rh(2)	2.734(1)	Rh(1)–Rh(3)	2.739(1)	Rh(3)–Ru	2.711(1)	Rh(3)–C(31)	2.220(4)
Rh(1)–Ru	2.620(1)	Rh(1)–C(11)	2.274(4)	Rh(3)–C(32)	2.249(4)	Rh(3)–C(33)	2.285(4)
Rh(1)–C(12)	2.287(4)	Rh(1)–C(13)	2.275(4)	Rh(3)–C(34)	2.279(4)	Rh(3)–C(35)	2.239(4)
Rh(1)–C(14)	2.255(4)	Rh(1)–C(15)	2.254(4)	Rh(3)–C(4)	2.147(5)	Rh(3)–C(5)	2.053(5)
Rh(1)–C(4)	1.971(5)	Rh(2)–Rh(3)	2.684(1)	Ru–C(1)	1.910(7)	Ru–C(2)	1.897(7)
Rh(2)–Ru	2.715(1)	Rh(2)–C(21)	2.267(4)	Ru–C(3)	1.905(7)	Ru–C(5)	2.214(5)
Rh(2)–C(22)	2.227(4)	Rh(2)–C(23)	2.217(4)	C(1)–O(1)	1.127(10)	C(2)–O(2)	1.135(9)
Rh(2)–C(24)	2.252(4)	Rh(2)–C(25)	2.282(4)	C(3)–O(3)	1.134(9)	C(4)–O(4)	1.187(6)
Rh(2)–C(4)	2.176(5)	Rh(2)–C(5)	2.028(5)	C(5)–O(5)	1.195(7)		
Rh(2)–Rh(1)–Rh(3)	58.7(1)	Rh(2)–Rh(1)–Ru	60.9(1)	Rh(1)–Ru–C(2)	85.3(2)	Rh(2)–Ru–C(2)	89.0(2)
Rh(3)–Rh(1)–Ru	60.7(1)	Rh(2)–Rh(1)–C(4)	52.1(1)	Rh(3)–Ru–C(2)	141.8(2)	C(1)–Rh–C(2)	95.7(3)
Rh(3)–Rh(1)–C(4)	51.1(1)	Ru–Rh(1)–C(4)	100.5(1)	Rh(1)–Ru–C(3)	89.5(2)	Rh(2)–Ru–C(3)	147.3(2)
Rh(1)–Rh(2)–Rh(3)	60.7(1)	Rh(1)–Rh(2)–Ru	57.5(1)	Rh(3)–Ru–C(3)	94.6(2)	C(1)–Ru–C(3)	92.2(3)
Rh(3)–Rh(2)–Ru	60.3(1)	Rh(1)–Rh(2)–C(4)	45.6(1)	C(2)–Ru–C(3)	104.6(3)	Rh(1)–Ru–C(5)	96.1(1)
Rh(3)–Rh(2)–C(4)	51.1(1)	Ru–Rh(2)–C(4)	92.5(1)	Rh(2)–Ru–C(5)	47.2(1)	Rh(3)–Ru–C(5)	48.0(1)
Rh(1)–Rh(2)–C(5)	97.3(2)	Rh(3)–Rh(2)–C(5)	49.3(2)	C(1)–Ru–C(5)	81.7(3)	C(2)–Ru–C(5)	125.2(3)
Ru–Rh(2)–C(5)	53.2(2)	C(4)–Rh(2)–C(5)	100.2(2)	C(3)–Ru–C(5)	130.2(3)	Ru–C(1)–O(1)	179.4(10)
Rh(1)–Rh(3)–Rh(2)	60.5(1)	Rh(1)–Rh(3)–Ru	57.5(1)	Ru–C(2)–O(2)	176.6(6)	Ru–C(3)–O(3)	178.5(6)
Rh(2)–Rh(3)–Ru	60.4(1)	Rh(1)–Rh(3)–C(4)	45.6(1)	Rh(1)–C(4)–Rh(2)	82.3(2)	Rh(1)–C(4)–Rh(3)	83.3(2)
Rh(2)–Rh(3)–C(4)	52.1(1)	Ru–Rh(3)–C(4)	93.3(1)	Rh(2)–C(4)–Rh(3)	76.8(2)	Rh(1)–C(4)–O(4)	135.7(4)
Rh(1)–Rh(3)–C(5)	96.5(2)	Rh(2)–Rh(3)–C(5)	48.5(1)	Rh(2)–C(4)–O(4)	127.9(4)	Rh(3)–C(4)–O(4)	130.1(4)
Ru–Rh(3)–C(5)	53.2(2)	C(4)–Rh(3)–C(5)	100.3(2)	Rh(2)–C(5)–Rh(3)	82.3(2)	Rh(2)–C(5)–Ru	79.5(2)
Rh(1)–Ru–Rh(2)	61.6(1)	Rh(1)–Ru–Rh(3)	61.8(1)	Rh(3)–C(5)–Ru	78.8(2)	Rh(2)–C(5)–O(5)	133.5(4)
Rh(2)–Ru–Rh(3)	59.3(1)	Rh(1)–Ru–C(1)	177.8(2)	Rh(3)–C(5)–O(5)	132.1(4)	Ru–C(5)–O(5)	130.0(4)
Rh(2)–Ru–C(1)	116.3(2)	Rh(3)–Ru–C(1)	116.6(2)				

* Estimated standard deviations (e.s.d.s) are given in parentheses in Tables 1—4.

Table 2. Selected internuclear distances (Å) and angles (°) for the complex $[RuRh_2(\mu\text{-}CO)(\mu_3\text{-}CO)(CO)_2(\eta^4\text{-}C_8H_{10})(\eta\text{-}C_5Me_5)_2]$ (**2**)

Rh(1)–Rh(2)	2.672(1)	Rh(1)–Ru	2.815(1)	Ru–C(34)	2.188(4)	C(1)–O(1)	1.187(4)
Rh(1)–C(1)	2.038(4)	Rh(1)–C(3)	1.989(3)	C(2)–O(2)	1.148(5)	C(3)–O(3)	1.170(5)
Rh(2)–Ru	2.766(1)	Rh(2)–C(1)	2.069(4)	C(4)–O(4)	1.143(6)	C(30)–C(31)	1.502(7)
Rh(2)–C(2)	2.412(5)	Rh(2)–C(3)	2.000(4)	C(30)–C(35)	1.542(6)	C(30)–C(37)	1.546(7)
Ru–C(1)	2.247(4)	Ru–C(2)	1.930(4)	C(31)–C(32)	1.409(7)	C(32)–C(33)	1.412(6)
Ru–C(4)	1.898(4)	Ru–C(31)	2.238(4)	C(33)–C(34)	1.415(7)	C(34)–C(35)	1.516(7)
Ru–C(32)	2.185(4)	Ru–C(33)	2.165(4)	C(35)–C(36)	1.552(7)	C(36)–C(37)	1.529(7)
Ru(2)–Rh(1)–Ru	60.5(1)	Rh(2)–Rh(1)–C(1)	49.9(1)	Rh(2)–Ru–C(2)	58.6(1)	C(1)–Ru–C(2)	106.0(2)
Ru–Rh(1)–C(1)	52.2(1)	Rh(2)–Rh(1)–C(3)	48.1(1)	Rh(1)–Ru–C(4)	68.2(1)	Rh(2)–Ru–C(4)	113.3(1)
Ru–Rh(1)–C(3)	81.9(1)	C(1)–Rh(1)–C(3)	97.6(2)	C(1)–Ru–C(4)	111.5(2)	C(2)–Ru–C(4)	93.6(2)
Rh(1)–Rh(2)–Ru	62.3(1)	Rh(1)–Rh(2)–C(1)	48.9(1)	Rh(1)–C(1)–Rh(2)	81.2(1)	Rh(1)–C(1)–Ru	82.0(1)
Ru–Rh(2)–C(1)	53.0(1)	Rh(1)–Rh(2)–C(2)	88.0(1)	Rh(2)–C(1)–Ru	79.6(1)	Rh(1)–C(1)–O(1)	131.1(3)
Ru–Rh(2)–C(2)	43.1(1)	C(1)–Rh(2)–C(2)	96.1(1)	Rh(2)–C(1)–O(1)	131.5(3)	Ru–C(1)–O(1)	131.8(3)
Rh(1)–Rh(2)–C(3)	47.8(1)	Ru–Rh(2)–C(3)	83.0(1)	Rh(2)–C(2)–Ru	78.3(1)	Rh(2)–C(2)–O(2)	123.4(3)
C(1)–Rh(2)–C(3)	96.3(2)	C(2)–Rh(2)–C(3)	74.5(2)	Ru–C(2)–O(2)	158.1(4)	Rh(1)–C(3)–Rh(2)	84.1(1)
Rh(1)–Ru–Rh(2)	57.2(1)	Rh(1)–Ru–C(1)	45.8(1)	Rh(1)–C(3)–O(3)	138.2(3)	Rh(2)–C(3)–O(3)	137.3(3)
Rh(2)–Ru–C(1)	47.4(1)	Rh(1)–Ru–C(2)	94.6(1)	Ru–C(4)–O(4)	167.5(4)		

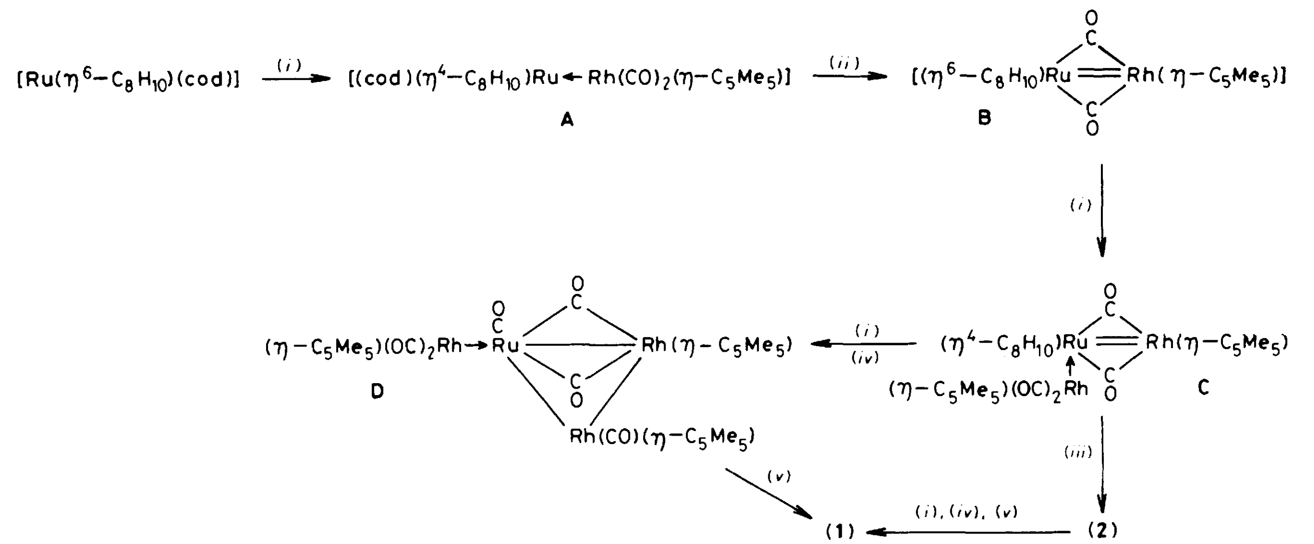
symmetrically bridges the Rh(1)–Rh(2) vector [Rh(1)–C(3)–O(3) 138.2(3), Rh(2)–C(3)–O(3) 137.3(3)°; Rh(1)–C(3) 1.989(3), Rh(2)–C(3) 2.000(4) Å]. The C(3)–O(3) and Rh(1)–Rh(2) vectors are at an angle of 89.7°, while the Rh(1)C(3)O(3)Rh(2) fragment is essentially planar, with the greatest deviation (0.037 Å) being shown by C(3). This plane is inclined at 71.4° to that of the metal triangle.

The carbonyl ligand C(1)O(1) caps the metal triangle, with some asymmetry reflected in the metal–carbon distances [Rh(1)–C(1) 2.038(4), Rh(2)–C(1) 2.069(4), Ru–C(1) 2.247(4) Å]. The C(1)–O(1) vector is almost perpendicular (93.4°) to the metal triangle. The C–O and C–Rh(Ru) distances are as expected, the greater being associated with C(1) and the least with C(4).

The geometry of the bicyclo[4.2.0]octa-2,4-diene ligand is very similar to that found for this group in the complex $[Fe(1\text{—}6\text{-}\eta\text{-}C_8H_{10})(1\text{—}4\text{-}\eta\text{-}[4.2.0]C_8H_{10})]$,[10] with extensive electron delocalisation within the C(31)–C(34) group [C(31)–C(32) 1.409(7), C(32)–C(33) 1.412(6), C(33)–C(34) 1.415(7) Å]. There is an approximate mirror plane through the midpoints of the vectors C(32)–C(33) and C(31)–C(34), and this plane is skewed relative to the RuRh(1)Rh(2) plane by 41°.

Compound (**2**), with its $Ru(CO)_2(\eta^4\text{-}C_8H_{10})$ (ML_4, d^8) fragment, is isolobal with several trimetal complexes in which 'carbene-like' metal–ligand groups are bonded to the inorganic 'alkene' $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$.[11] As such it is perhaps not surprising that the Rh–Rh distance [2.672(1) Å] in (**2**) is similar to that found in the related species $[MoRh_2(\mu\text{-}CO)_2(CO)_5(\eta\text{-}C_5Me_5)_2]$ [2.623(1) Å],[12] $[PtRh_2(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ [2.647(2) Å], and $[PtRh_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2][BF_4]$ [2.647(2) Å].[13] The Ru–Rh distances [2.815(1) and 2.766(1) Å] in (**2**) are appreciably longer than those in (**1**) (see above). Metal–metal separations in trimetal complexes are generally *ca.* 0.05—0.1 Å longer than those found in tetranuclear clusters.

Having established the structure of (**2**), the spectroscopic data



Scheme. C_8H_{10} = cyclo-octa-1,3,5-triene. (*i*) + [Rh(CO)$_2$(η-C$_5$Me$_5$)]; (*ii*) −cod; (*iii*) cyclo-octa-1,3,5-triene isomerises to bicyclo[4.2.0]octa-2,4-diene; (*iv*) −C_8H_{10}; (*v*) −CO

(Experimental section) for this compound can be interpreted. The four CO ligands give rise in the i.r. spectrum to four bands which may be assigned as follows: 1 937 (RuCO), 1 857 [RuCO ··· Rh(2)], 1 790 [Rh(μ-CO)Rh], and 1 667 cm^{-1} (μ$_3$-CO). In the ^{1}H n.m.r. spectrum, the signals for the η^4-C_8H_{10} ligand are remarkably similar to those observed in the spectra of other metal complexes containing the bicyclo[4.2.0]octa-2,4-diene ligand.[7] The ^{13}C-{^{1}H} n.m.r. data revealed that (**2**) undergoes dynamic behaviour in solution. When the spectrum is measured at room temperature there is only one very broad peak (δ 235 p.p.m.) for the CO groups implying site exchange of all these ligands on the n.m.r. time-scale with coalescence near the temperature of measurement. At −80 °C, however, separate signals due to the μ$_3$-CO, δ 250.2 p.p.m. [t, *J*(RhC) 34 Hz], and μ-CO, δ 245.0 p.p.m. [t, *J*(RhC) 44 Hz], ligands are observed. Nevertheless, even at −80 °C the carbonyl groups attached to the ruthenium atom give only one slightly broad resonance (δ 233.6 p.p.m.) and this, together with the observation of an apparent equivalence of the η-C$_5$Me$_5$ ligands, shows that the limiting spectrum at low temperatures had not been reached. In the structure of (**2**), established by *X*-ray diffraction, the orientation of the η-C_8H_{10} ligand and the presence of the semi-bridging C(2)O(2) group makes the Rh(1)(η-C$_5$Me$_5$) and Rh(2)(η-C$_5$Me$_5$) sites inequivalent. The dynamic process still persisting at −80 °C probably involves rotation of the Ru(CO)$_2$(η-C_8H_{10}) fragment about an axis through the ruthenium atom and the midpoint of the Rh(1)–Rh(2) vector with concomitant exchange between the terminal and semi-bridging carbonyl ligands. The mechanism would be similar to rotation of the Mo(CO)$_5$ group in the compound [MoCoRh(μ-CO)$_2$(CO)$_5$(η-C$_5$Me$_5$)$_2$].[12]

The formation of compounds (**1**) and (**2**) in the reaction between [Rh(CO)$_2$(η-C$_5$Me$_5$)] and [Ru(η^6-C_8H_{10})(cod)] must occur *via* a complex sequence of steps, but in agreement with earlier work, mentioned in the Introduction, the two products obtained contain RuCO groups; carbonyl groups having been transferred from rhodium, as expected. There is insufficient information available to be sure of the pathway followed, nevertheless the known behaviour of the reactants in other situations may provide a clue. The compound [Ru(η^6-C_8H_{10})(cod)] is known[14] to react with the donor molecule CO in a first-order reaction to give an adduct [Ru(CO)(η^4-C_8H_{10})(cod)], corresponding to 'slippage' of the cyclo-octa-1,3,5-triene ligand from an η^6- to an η^4-bonding mode. The rhodium compounds [RhL$_2$(η-C$_5$R$_5$)] [L = CO or PR'$_3$ (R' = alkyl or aryl), R = H or Me] readily function as donor molecules forming heteronuclear metal–metal bonds with other groups,[15,16] in accord with a metal-centred lone pair of electrons.[17] It is possible, therefore, that the reactants combine to form an intermediate **A** (Scheme), with a rhodium–ruthenium donor bond, in a process made possible by slippage of the cyclo-octa-1,3,5-triene ligand.[7] This transformation could be reversed in the formation of **B**, a species isolobal with the known compound [CoRh(μ-CO)$_2$(η-C$_5$Me$_5$)$_2$].[18] Complex (**2**) could then form *via* **C**, the cyclo-octa-1,3,5-triene again undergoing slippage in order to accommodate another [Rh(CO)$_2$(η-C$_5$Me$_5$)] molecule, while rearranging to the bicyclo[4.2.0]octa-2,4-diene moiety. Displacement of the cyclo-octatriene ligand from **C** by [Rh(CO)$_2$(η-C$_5$Me$_5$)] could afford **D**, which with a 16-electron ruthenium centre could rearrange to give (**1**). It was established that (**1**) is formed when (**2**) is heated with [Rh(CO)$_2$(η-C$_5$Me$_5$)] but this process proceeds only slowly above 80 °C. Hence this cannot be the major pathway to (**1**).

Experimental

Light petroleum refers to that fraction of b.p. 40—60 °C. Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. All solvents were rigorously dried before use. The n.m.r. measurements were made with JNM-FX 90Q and FX 200 instruments, and measured in CDCl$_3$ (^{1}H) or CD$_2$Cl$_2$—CH$_2$Cl$_2$ (^{13}C-{^{1}H}). I.r. spectra were recorded in light petroleum with a Nicolet 10-MX FT spectrophotometer. The compounds [Rh(CO)$_2$(η-C$_5$Me$_5$)][19] and [Ru(η^6-C_8H_{10})(cod)][3] were prepared as previously described.

Reaction between [Rh(CO)$_2$(η-C$_5$Me$_5$)] *and* [Ru(η^6-C_8H_{10})(cod)].—A toluene (10 cm^3) solution of [Ru(η^6-C_8H_{10})(cod)] (0.32 g, 1.0 mmol) and [Rh(CO)$_2$(η-C$_5$Me$_5$)] (0.59 g, 2.0 mmol) was heated at 60 °C for 48 h, after which time i.r. measurements revealed that all of the reactants had been consumed. Solvent was removed *in vacuo*, and a slurry of the residue in light petroleum was transferred to a chromatography

Table 3. Atomic positional parameters (fractional co-ordinates) ($\times 10^4$) for complex (**1**)

Atom	x	y	z	Atom	x	y	z
Rh(1)	3 075(1)	6 625(1)	4 294	C(224)	8 416(6)	7 144(6)	3 613(3)
Rh(2)	5 395(1)	6 759(1)	3 780(1)	C(225)	6 555(8)	8 519(4)	3 396(5)
Rh(3)	4 997(1)	6 861(1)	5 209(1)	C(31)*	6 003(4)	6 687(2)	6 237(2)
Ru	4 619(1)	5 502(1)	4 522(1)	C(32)	6 428	7 385	5 925
C(11)*	1 504(4)	6 423(3)	3 518(2)	C(33)	5 443	7 912	5 904
C(12)	1 308	5 952	4 135	C(34)	4 408	7 541	6 203
C(13)	1 172	6 443	4 744	C(35)	4 754	6 784	6 408
C(14)	1 284	7 217	4 503	C(331)	6 770(7)	5 991(4)	6 414(4)
C(15)	1 490	7 204	3 745	C(332)	7 699(6)	7 554(5)	5 687(4)
C(111)	1 517(8)	6 176(6)	2 738(5)	C(333)	5 523(10)	8 742(4)	5 670(5)
C(112)	1 027(7)	5 095(4)	4 106(6)	C(334)	3 220(9)	7 919(6)	6 348(5)
C(113)	807(8)	6 189(6)	5 492(5)	C(335)	3 989(8)	6 220(5)	6 839(4)
C(114)	1 058(8)	7 937(5)	4 951(6)	C(1)	5 796(7)	4 712(4)	4 684(5)
C(115)	1 512(7)	7 908(5)	3 292(7)	O(1)	6 491(7)	4 246(4)	4 785(6)
C(21)*	5 390(3)	7 430(2)	2 728(2)	C(2)	4 016(7)	5 087(4)	3 644(4)
C(22)	5 590	6 636	2 587	O(2)	3 680(8)	4 804(4)	3 128(3)
C(23)	6 700	6 420	2 923	C(3)	3 567(6)	5 101(4)	5 249(4)
C(24)	7 185	7 081	3 272	O(3)	2 939(5)	4 848(4)	5 673(3)
C(25)	6 375	7 705	3 151	C(4)	4 168(4)	7 523(3)	4 361(3)
C(221)	4 378(8)	7 928(4)	2 433(4)	O(4)	4 062(4)	8 200(2)	4 297(3)
C(222)	4 879(8)	6 144(5)	2 061(4)	C(5)	6 248(5)	6 243(3)	4 623(3)
C(223)	7 304(8)	5 653(4)	2 874(5)	O(5)	7 282(4)	6 074(3)	4 740(2)

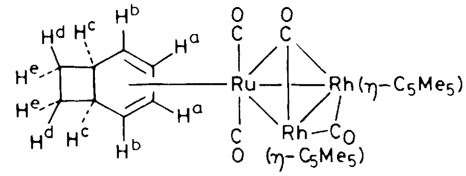
* Pivot atom of a rigid group. Other atoms in the group have identical e.s.d.s.

Table 4. Atomic positional parameters (fractional co-ordinates) ($\times 10^4$) for complex (**2**)

Atom	x	y	z	Atom	x	y	z
Rh(1)	800(1)	1 048(1)	2 999(1)	C(19)	−306(14)	1 145(4)	4 871(5)
Rh(2)	1 420(1)	1 531(1)	1 584(1)	C(20)	3 661(4)	1 304(2)	1 207(3)
Ru	22(1)	2 312(1)	2 571(1)	C(21)	2 411(5)	974(2)	675(2)
C(1)	2 233(4)	1 767(2)	2 830(2)	C(22)	1 415(5)	1 432(2)	213(2)
C(2)	−939(5)	2 122(2)	1 425(2)	C(23)	2 003(5)	2 032(2)	483(2)
C(3)	−159(4)	912(2)	1 797(2)	C(24)	3 416(4)	1 957(2)	1 089(3)
C(4)	−1 525(5)	1 900(2)	3 024(2)	C(25)	5 032(5)	1 004(3)	1 748(3)
O(1)	3 481(3)	1 901(1)	3 201(2)	C(26)	2 283(6)	270(2)	569(3)
O(2)	−1 821(4)	2 153(2)	805(2)	C(27)	12(5)	1 302(3)	−460(3)
O(3)	−1 088(4)	584(2)	1 398(2)	C(28)	1 353(6)	2 650(2)	115(3)
O(4)	−2 574(4)	1 759(2)	3 290(2)	C(29)	4 472(6)	2 472(2)	1 499(3)
C(10)	−251(6)	320(3)	3 719(3)	C(30)	−139(5)	3 196(2)	4 057(3)
C(11)	889(8)	41(2)	3 367(3)	C(31)	1 093(5)	2 856(2)	3 721(3)
C(12)	2 296(6)	300(3)	3 729(4)	C(32)	1 582(5)	3 095(2)	3 009(3)
C(13)	2 065(7)	748(3)	4 303(3)	C(33)	413(6)	3 301(2)	2 342(3)
C(14)	481(8)	775(3)	4 289(3)	C(34)	−1 093(5)	3 238(2)	2 491(3)
C(15)	−1 912(7)	127(5)	3 539(6)	C(35)	−1 422(5)	3 430(2)	3 337(3)
C(16)	693(14)	−501(3)	2 758(4)	C(36)	−1 038(7)	4 123(2)	3 615(4)
C(17)	3 829(9)	94(5)	3 551(7)	C(37)	215(6)	3 888(2)	4 336(3)
C(18)	3 283(13)	1 135(4)	4 863(5)				

column (2 × 20 cm) charged with alumina. Elution with dichloromethane–light petroleum (1:9) gave firstly a purple eluate which on slow evaporation of solvent afforded purple *crystals* of $[RuRh_3(\mu_3\text{-}CO)_2(CO)_3(\eta\text{-}C_5Me_5)_3]$ (**1**) (0.15 g, 16% based on ruthenium consumed) (Found: C, 43.6; H, 4.9. $C_{35}H_{45}O_5Rh_3Ru$ requires C, 44.0; H, 4.7%); $\nu_{max.}$(CO) at 2 008s, 1 946m, 1 931m, 1 690w, and 1 667m cm^{-1}. N.m.r.: ^1H, δ 1.65 (s, 45 H, C_5Me_5); $^{13}C\text{-}\{^1H\}$, δ 245.7 [q, μ_3-CO, *J*(RhC) 37], 223.2 [t, μ_3-CO, *J*(RhC) 12 Hz], 197.9 (s, RuCO), 101.2 (C_5Me_5), and 9.9 p.p.m. (C_5*Me*$_5$).

The second eluate from the column was green in colour, and reduction in volume of solvent and cooling to −20 °C gave green *crystals* of $[RuRh_2(\mu\text{-}CO)(\mu_3\text{-}CO)(CO)_2(\eta^4\text{-}C_8H_{10})(\eta\text{-}C_5Me_5)_2]$ (**2**) (0.11 g, 14%) (Found: C, 48.6; H, 5.4. Calc. for $C_{32}H_{40}O_4Rh_2Ru$: C, 48.4; H, 5.1%); $\nu_{max.}$(CO) at 1 937s br, 1 857m br, 1 790s, and 1 667s cm^{-1}. N.m.r.: ^1H, δ 1.10 (m, 2 H^d or H^e), 1.66 (s, 30 H, C_5Me_5), 1.84 (m, 2 H^e or H^d), 2.56 (m, 2 H^c), 3.42 (m, 2 H^b), and 5.08 (m, 2 H^a); $^{13}C\text{-}\{^1H\}$ (−80 °C), δ 250.2 [t, μ_3-CO, *J*(RhC) 34], 245.0 [t, μ-CO, *J*(RhC) 44 Hz], 103.9 (C_5Me_5), 94.2 (C^a), 72.5 (C^b), 39.9 (C^c), 25.2 (C^d), and 8.7 p.p.m.



(C_5*Me*$_5$). The assignments for C^a–C^d were confirmed by off-resonance experiments and by correlations of the shifts observed previously for metal complexes containing the bicyclo[4.2.0]cyclo-octa-1,4-diene ligand.[7]

Crystal Structure Determination of Complex (**1**).—A suitable purple crystal of (**1**) (*ca.* 0.45 × 0.45 × 0.13 mm) was grown from dichloromethane–light petroleum. Diffracted intensities were collected on a Nicolet *P3m* diffractometer using the θ—2θ scan mode ($3 \leqslant 2\theta \leqslant 55°$).

Crystal data. $C_{35}H_{45}O_5Rh_3Ru$, $M = 955.6$, orthorhombic, $a = 11.002(6)$, $b = 17.353(9)$, $c = 18.492(9)$ Å, $U = 3\,531(4)$ Å^3, $Z = 4$, $D_c = 1.80$ g cm^{-3}, $F(000) = 1\,896$, space group $Pbn2_1$ (non-standard setting of $Pna2_1$, no. 33) Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 18.1 cm^{-1}.

Data were corrected for Lorentz and polarisation effects, and an empirical correction was applied for *X*-ray absorption.[20] Of 4 612 reflections, 3 902 independent intensities had $I \geqslant 2.5\sigma(I)$ and only these were used for the structure solution and refinement. The structure was solved by conventional heavy-atom and electron-density difference methods and was refined by blocked-cascade full-matrix least squares, with anisotropic thermal parameters for all non-hydrogen atoms. The C_5Me_5 rings were treated as rigid groups (C–C 1.420 Å), and the methyl hydrogen atoms were included at calculated positions (C–H 0.960 Å) with common refined isotropic thermal parameters. A weighting scheme of the form $w = [\sigma^2(F_o) + 0.001|F_o|^2]^{-1}$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks > 0.8 e Å^{-3} except in the immediate neighbourhood of the metal atoms. Refinement led to $R = 0.025$ ($R' = 0.027$). Scattering factors were from ref. 21. All computations were carried out on an 'Eclipse' Data General computer with the SHELXTL system of programs.[20] Table 3 lists the atomic co-ordinates.

Crystal Structure Determination of Complex (**2**).—Dark green crystals of (**2**) were grown from dichloromethane–light petroleum, and that chosen for study was an irregular prism of dimensions *ca.* 0.5 × 0.5 × 0.1 mm. Data were collected as described above, using the ω-scan mode in the range $3 \leqslant 2\theta \leqslant 50°$. Of the 5 278 unique reflections, 4 491 with $I \geqslant 2.5\sigma(I)$ were used for structure solution and refinement after corrections for Lorentz, polarisation, and absorption effects.

Crystal data. $C_{32}H_{40}O_4Rh_2Ru$, $M = 795$, monoclinic, $a = 8.897(2)$, $b = 21.162(5)$, $c = 16.246(6)$ Å, $\beta = 101.56(2)°$, $U = 2\,997(2)$ Å^3, $Z = 4$, $D_c = 1.76$ g cm^{-3}, $F(000) = 1\,536$, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), μ(Mo-K_α) = 15.9 cm^{-1}.

The structure solution and refinement were similar to that described above for (**1**), except that no geometric constraints were applied to the C_5Me_5 rings and the methyl hydrogens were included at calculated positions with isotropic thermal parameters *ca.* 1.2 times the equivalent isotropic thermal parameters of the parent carbon atoms. The hydrogen atoms of the η^4-C_8H_{10} ligand were, however, located from an electron-density difference synthesis, but were refined with isotropic thermal parameters and constrained positional parameters (C–H 0.960 Å). A weighting scheme of the form $w = [\sigma^2(F_o) + 0.000\,11|F_o|^2]^{-1}$ gave a satisfactory weight analysis. Convergence was reached at $R = 0.029$ ($R' = 0.031$) with a final electron-density difference showing no residual peaks > 0.57 or < −0.49 e Å^{-3} except in the vicinity of the metal atoms. Scattering factors, corrections for anomalous dispersion,[21] and all calculations[20] were as for (**1**). The atomic positional parameters for (**2**) are given in Table 4.

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