Structural Comparison of Cluster Compounds containing an Edge-bridging $M(PPh_3)$ (M = Cu, Ag, or Au) Fragment. *X*-Ray Crystal Structure of $[AgRu_3(CO)_9(C_2Bu^t)(PPh_3)]$†

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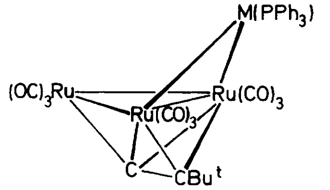
An *X*-ray diffraction study of $[AgRu_3(CO)_9(C_2Bu^t)(PPh_3)]$ shows that the cluster adopts a 'butterfly' metal-core structure, with the silver atom occupying a 'wing-tip' site. The t-butylacetylide ligand lies on the convex side of the 'butterfly' metal core, interacting with all three ruthenium atoms *via* one σ bond to the 'wing-tip' ruthenium site and two π bonds to the ruthenium atoms which form the 'hinge' of the 'butterfly'. Comparison of the structure with those reported for the analogous copper- and gold-containing species reveals that the M–P and M–Ru bond lengths are markedly longer for M = Ag than for M = Cu or Au.

The chemistry of mixed-metal cluster compounds is attracting considerable current interest, but detailed structural investigations of those containing one or more $Ag(PR_3)$ units are relatively rare.[1-3] The first comparative study of the effect of the nature of all three Group 1B metals on the structure of a series of related cluster compounds containing edge-bridging $M(PR_3)$ (M = Cu, Ag, or Au; R = alkyl or aryl) fragments has recently been reported by Bruce *et al.*[1] Their *X*-ray diffraction studies of the Group 1B metal clusters $[MRu_3(\mu_3\text{-}PhPCH_2PPh_2)(CO)_9(PPh_3)]$ (M = Cu, Ag, or Au) show 'butterfly' metal-core geometries with the coinage metal occupying a 'wing-tip' site. Interestingly, the Ag–P distance [2.422(3) Å] was found to be very long compared not only to Cu–P [2.228(2) Å] but also to Au–P [2.297(2) Å] and furthermore, the mean M–Ru distances are significantly longer for M = Ag than for M = Cu or Au [2.787(1), 2.603(1), and 2.760(1) Å, respectively]. Similar 'butterfly' skeletal geometries have previously been reported for the two mixed-metal clusters $[MRu_3(CO)_9(C_2Bu^t)(PPh_3)]$ [M = Cu (**1**)[4] or Au (**3**)[5]]. The present *X*-ray diffraction study of $[AgRu_3(CO)_9(C_2Bu^t)(PPh_3)]$ (**2**) completes the structural data for this series of analogous clusters, and allows detailed comparison of the structures for all three metals. It shows that the interesting trends observed in the earlier series[1] are also present here, as once again all bonds from the silver atom are markedly longer than the equivalent distances from copper or gold.



	M
(**1**)	Cu
(**2**)	Ag
(**3**)	Au

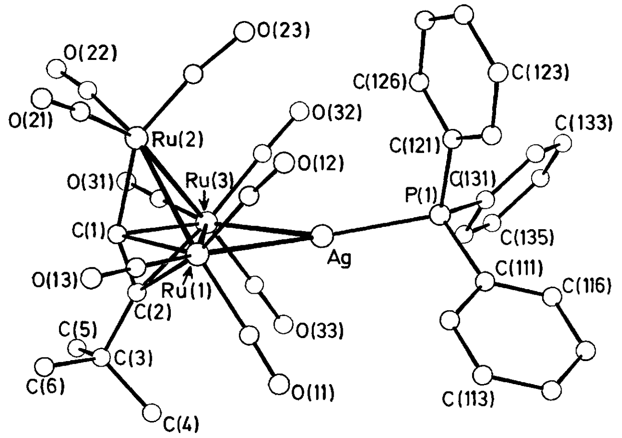


Figure. Molecular structure of $[AgRu_3(CO)_9(C_2Bu^t)(PPh_3)]$ (**2**), showing the crystallographic numbering. The carbon atom of each carbonyl group has the same number as the oxygen atom

Results and Discussion

X-Ray structure analysis shows that $[AgRu_3(CO)_9(C_2Bu^t)(PPh_3)]$ (**2**) adopts a similar 'butterfly' metal-core structure to those previously established for the analogous copper (**1**)[4] and gold (**3**)[5] species, with the heterometal atom in a 'wing-tip' site (Figure). The dihedral angle between the 'wings' of the 'butterfly' [Ru(1)–Ru(2)–Ru(3) and Ru(1)–Ru(3)–Ag] is 120.6°, which is intermediate in value between that of 115.7 in (**1**) and 129.3° in (**3**). The heteronuclear clusters (**1**)—(**3**) may all formally be envisaged as derived from $[Ru_3(\mu\text{-}H)(CO)_9(C_2Bu^t)]$ (**4**)[6] by replacement of the μ-H ligand by a bridging $M(PPh_3)$ fragment. Table 1 summarises the principal bond lengths for (**2**), and those reported for the related structures (**1**), (**3**), (**4**), and the parent monoanion $[Ru_3(CO)_9(C_2Bu^t)]^-$ (**5**)[7] are also included for comparison. Table 2 lists selected bond angles for (**2**).

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† 1,1,1,2,2,2,3,3,3-Nonacarbonyl-μ_3-[t-butylethynyl-C^1-(Ru^{1-3}),$C^2(Ru^{1,2})$]-1,2-μ-[(triphenylphosphine)argentio]-*triangulo*-triruthenium.

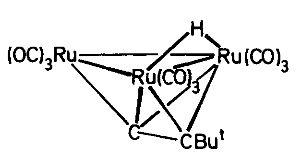
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Selected bond lengths (Å) for [$AgRu_3(CO)_9(C_2Bu^t)(PPh_3)$] (**2**) compared with those of the related compounds [$MRu_3(CO)_9(C_2Bu^t)(PPh_3)$] [M = Cu (**1**) or Au (**3**)], [$Ru_3(\mu\text{-}H)(CO)_9(C_2Bu^t)$] (**4**), and [$Ru_3(CO)_9(C_2Bu^t)$]$^-$(**5**) (renumbered where necessary)

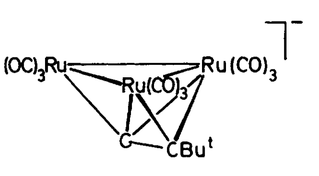
Bond distances	(**1**)[4]	(**2**)	(**3**)[5]	(**4**)[6]	(**5**)[7]
Ru(1)–Ru(2)	2.819(1)	2.814(3)	2.800(1)	2.799(3)	2.800(3)
Ru(1)–Ru(3)	2.762(1)	2.805(2)	2.820(1)	2.792(3)	2.665(3)
Ru(2)–Ru(3)	2.808(1)	2.799(3)	2.786(1)	2.795(3)	2.790(3)
Ru(1)–M	2.603(1)	2.788(3)	2.763(1)	—	—
Ru(3)–M	2,603(1)	2.785(3)	2.757(1)	—	—
M–P(1)	2.217(2)	2.405(9)	2.276(3)	—	—
Ru(1)–C(1)	2.203(6)	2.20(3)	2.22(1)	2.214(3)	2.18(2)
Ru(2)–C(1)	1.945(7)	2.02(3)	1.95(2)	1.947(3)	1.95(2)
Ru(3)–C(1)	2.211(7)	2.23(3)	2.19(1)	2.207(3)	2.16(2)
Ru(1)–C(2)	2.260(7)	2.27(3)	2.21(1)	2.271(3)	2.24(2)
Ru(3)–C(2)	2.259(6)	2.25(2)	2.27(1)	2.268(3)	2.24(2)
C(1)–C(2)	1.313(9)	1.28(4)	1.29(2)	1.315(3)	1.27(3)

Table 2. Selected bond angles (°) for [$AgRu_3(CO)_9(C_2Bu^t)(PPh_3)$] (**2**)

Ag–Ru(1)–Ru(2)	97.2(1)	Ag–Ru(1)–Ru(3)	59.7(1)
Ag–Ru(3)–Ru(1)	59.8(1)	Ag–Ru(3)–Ru(2)	97.7(1)
Ru(3)–Ag–Ru(1)	60.4(1)	Ru(3)–Ru(1)–Ru(2)	59.8(1)
Ru(3)–Ru(2)–Ru(1)	60.0(1)	Ru(2)–Ru(3)–Ru(1)	60.3(1)
P(1)–Ag–Ru(1)	145.5(2)	P(1)–Ag–Ru(3)	151.3(2)
C(1)–Ru(1)–Ru(2)	45.5(7)	C(1)–Ru(1)–Ru(3)	51.1(7)
C(1)–Ru(1)–Ag	110.7(7)	C(1)–Ru(1)–C(11)	128(1)
C(1)–Ru(1)–C(12)	131(1)	C(1)–Ru(1)–C(13)	92(1)
C(2)–Ru(1)–Ru(2)	77.5(6)	C(2)–Ru(1)–Ru(3)	51.3(5)
C(2)–Ru(1)–Ag	102.0(7)	C(2)–Ru(1)–C(11)	95(1)
C(2)–Ru(1)–C(12)	160.6(8)	C(2)–Ru(1)–C(13)	99(1)
C(2)–Ru(1)–C(1)	33(1)	C(1)–Ru(2)–Ru(1)	51.0(7)
C(1)–Ru(2)–Ru(3)	52.0(8)	C(1)–Ru(2)–Ru(3)	52.0(8)
C(1)–Ru(3)–Ru(1)	50.3(6)	C(1)–Ru(3)–Ru(2)	45.7(8)
C(1)–Ru(3)–Ag	110.0(7)	C(2)–Ru(3)–Ru(1)	51.8(7)
C(2)–Ru(3)–Ru(2)	78.1(7)	C(2)–Ru(3)–Ag	102.6(6)
C(2)–Ru(3)–C(1)	33(1)	Ru–C–O range	173(3)—179(3)



(**4**)



(**5**)

The present study shows that in the silver cluster (**2**), as in all the compounds included in Table 1, the t-butylacetylide ligand lies on the convex side of the 'butterfly' metal core, interacting with all three ruthenium atoms *via* one σ bond to the 'wing-tip' atom [Ru(2)–C(1) 2.02(3) Å] and two π bonds, one to each of the atoms forming the 'hinge' of the 'butterfly' [Ru(1)–C(1) 2.20(3), Ru(1)–C(2) 2.27(3), Ru(3)–C(1) 2.23(3), and Ru(3)–C(2) 2.25(2) Å]. These bond lengths for (**2**) do not differ significantly from those reported for the related compounds (**1**), and (**3**)—(**5**) (Table 1). Each ruthenium atom in (**2**) has three essentially linear carbonyl ligands [Ru–C–O 173(3)—179(3)°]. An extremely short contact occurs between one of these ligands and the silver atom [Ag ⋯ C(32) 2.69(2) Å], which is very similar to a contact present in a disilver hexanuclear cluster [$Ag_2Ru_4(CO)_{13}(PPh_3)_2$] [Ag(1) ⋯ C(32) 2.694(3) Å].[2] This type of Group 1B metal to carbonyl interaction is also a feature of a number of copper[4,8] and gold[9] mixed-metal clusters, and in the gold and copper analogues of (**2**), the same carbonyl ligand makes a short contact with the heterometal atom [Cu ⋯ C 2.469(7)[4] in (**1**) and Au ⋯ C 2.69(1)[5] Å in (**3**)].

In the silver compound (**2**), the lengths of the chemically equivalent bonds Ru(1)–Ru(2) and Ru(2)–Ru(3) [2.814(3) and 2.799(3) Å respectively] are significantly different. There is no obvious reason for this, but interestingly a slight asymmetry also occurs in the reported structures of not only the copper (**1**) and gold (**3**) compounds, but also in the related monoanion (**5**), where the Ru(1)–Ru(2) bonds are longer than the Ru(2)–Ru(3) bonds by 0.011, 0.014, and 0.010 Å respectively (Table 1).

The chemically unique Ru(1)–Ru(3) bond of length 2.665(3) Å reported for the 'parent' monoanion (**5**)[7] is very much shorter than the mean of the other two Ru–Ru bonds [2.795(2) Å]. In complex (**2**), the silver-bridged Ru(1)–Ru(3) bond [2.805(2) Å] is markedly elongated compared to the equivalent distance in (**5**), and is very close to the mean lengths of the other two unbridged Ru–Ru bonds [2.807(3) Å]. This observation is very similar to that reported for the analogous monohydrido species (**4**), where the hydrido-bridged Ru(1)–Ru(3) bond length [2.792(2) Å] is also longer than the equivalent distance in the monoanion (**5**), and is similar to the remaining Ru–Ru lengths [mean 2.797(2) Å].[6] In contrast to the silver cluster (**2**), the bridged bond Ru(1)–Ru(3) in the copper compound (**1**) is markedly shorter (0.052 Å)[4] and that in the gold complex (**3**) is longer (0.027 Å)[5] than the mean of the other two Ru–Ru bonds. Thus, the length of the 'hinge' bond, bridged by M(PPh_3), increases with increasing atomic number of the Group 1B metal in the order Cu < Ag < Au.

The most interesting feature of the present study is that the mean Ag–Ru length of 2.787(3) Å in (**2**) is not only very much longer than the mean Cu–Ru distance of 2.603(2) Å reported in (**1**),[4] but also considerably longer than the mean Au–Ru distance of 2.760(1) Å in (**3**).[5] This structural trend is also reflected in the M–P bond lengths, with the Ag–P bond [2.405(9) Å in (**2**)] being considerably longer than both the Cu–P and Au–P distances [2.217(2) in (**1**) and 2.276(3) Å in (**3**) respectively].

These results closely parallel those observed by Bruce *et al.*[1] for the series [$MRu_3(\mu_3\text{-}PhPCH_2PPh_2)(CO)_9(PPh_3)$] (see above), in which all the bonds from the silver are markedly longer than the equivalent distances from both copper and gold, and they indicate that these structural features may be a general characteristic of mixed-metal clusters containing an edge-bridging M(PR_3) (R = alkyl or aryl) unit.

Experimental

The cluster [$AgRu_3(CO)_9(C_2Bu^t)(PPh_3)$] (**2**) was prepared as previously described[4] and crystals suitable for *X*-ray diffraction studies were grown from a light petroleum (b.p. 40—60 °C) solution by slow evaporation and subsequent cooling to −20 °C.

Crystal Data for (**2**).—$C_{33}H_{24}AgO_9PRu_3$, $M = 1\,006.17$, monoclinic, $a = 16.117(3)$, $b = 16.791(13)$, $c = 14.488(3)$ Å, $\beta = 110.97(2)°$, $U = 3\,661.1$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.80$ g cm^{-3}, $F(000) = 1\,984$, $\mu(\text{Mo-}K_\alpha) = 16.64$ cm^{-1}.

The methods of data collection and data processing were similar to those described previously.[10] The crystal selected for data collection had dimensions 0.44 × 0.48 × 0.21 mm. A scan width of 0.80° in θ was used to collect data in the θ range 3—25° by the ω/2θ technique. Equivalent reflections were merged to give 2 442 data with $I/\sigma(I) > 3.0$. No absorption corrections were applied.

The positions of the metal atoms were deduced from a Patterson synthesis. The remaining non-hydrogen atoms were found from subsequent difference-Fourier syntheses. Anisotropic thermal parameters were assigned to the metal and

Table 3. Fractional atomic co-ordinates for $[\mathrm{AgRu_3(C_2Bu^t)(CO)_9(PPh_3)}]$ (**2**)

Atom	x	y	z	Atom	x	y	z
Ru(1)	−0.207 98(14)	0.203 14(15)	0.276 52(11)	C(111)	−0.469 7(14)	0.328 2(12)	0.417 4(10)
Ru(2)	−0.257 5(2)	0.121 56(15)	0.095 11(13)	C(112)	−0.385 2(14)	0.312 1(12)	0.486 0(10)
Ru(3)	−0.291 54(14)	0.284 81(14)	0.098 36(12)	C(113)	−0.360 5(14)	0.341 4(12)	0.582 2(10)
Ag	−0.369 10(14)	0.281 03(14)	0.241 98(12)	C(114)	−0.420 3(14)	0.387 0(12)	0.609 8(10)
P(1)	−0.496 0(5)	0.293 5(5)	0.291 3(4)	C(115)	−0.504 7(14)	0.403 1(12)	0.541 1(10)
C(11)	−0.191 9(19)	0.280 6(19)	0.378 1(17)	C(116)	−0.529 4(14)	0.373 8(12)	0.445 0(10)
O(11)	−0.178 4(15)	0.322 5(14)	0.444 7(14)	C(121)	−0.546 7(14)	0.197 0(10)	0.285 8(12)
C(12)	−0.285 8(18)	0.133 9(18)	0.305 6(16)	C(122)	−0.561 5(14)	0.162 3(10)	0.366 0(12)
O(12)	−0.329 9(17)	0.095 8(16)	0.330 5(14)	C(123)	−0.599 5(14)	0.086 7(10)	0.356 7(12)
C(13)	−0.114 4(24)	0.140 3(23)	0.341 7(21)	C(124)	−0.622 8(14)	0.045 8(10)	0.267 2(12)
O(13)	−0.049 4(18)	0.095 1(16)	0.384 9(15)	C(125)	−0.608 0(14)	0.080 5(10)	0.187 0(12)
C(21)	−0.197 0(26)	0.025 8(26)	0.135 1(22)	C(126)	−0.570 0(14)	0.156 1(10)	0.196 3(12)
O(21)	−0.150 9(18)	−0.031 2(18)	0.162 8(15)	C(131)	−0.585 2(15)	0.355 5(13)	0.212 9(13)
C(22)	−0.269 1(20)	0.109 4(20)	−0.037 6(19)	C(132)	−0.673 9(15)	0.336 5(13)	0.194 6(13)
O(22)	−0.270 6(14)	0.108 4(14)	−0.119 0(13)	C(133)	−0.741 5(15)	0.383 6(13)	0.130 7(13)
C(23)	−0.371 1(26)	0.080 8(22)	0.079 4(21)	C(134)	−0.720 3(15)	0.449 6(13)	0.085 0(13)
O(23)	−0.440 5(18)	0.056 0(16)	0.075 2(14)	C(135)	−0.631 6(15)	0.468 7(13)	0.103 3(13)
C(31)	−0.286 0(19)	0.303 5(21)	−0.024 4(19)	C(136)	−0.564 0(15)	0.421 6(13)	0.167 3(13)
O(31)	−0.284 4(15)	0.314 1(14)	−0.104 7(14)	C(1)	−0.168 7(17)	0.210 9(19)	0.146 1(15)
C(32)	−0.410 7(19)	0.256 3(16)	0.046 9(16)	C(2)	−0.145 8(16)	0.278 6(16)	0.189 0(14)
O(32)	−0.487 6(16)	0.243 1(13)	0.010 2(13)	C(3)	−0.064 8(20)	0.331 8(19)	0.214 9(17)
C(33)	−0.302 9(23)	0.390 8(24)	0.127 3(20)	C(4)	−0.070 1(24)	0.397 5(24)	0.286 8(21)
O(33)	−0.311 8(18)	0.457 6(19)	0.144 6(15)	C(5)	−0.068 4(24)	0.374 0(24)	0.113 0(21)
				C(6)	0.020 0(29)	0.275 0(28)	0.258 1(26)

phosphorus atoms during the final cycles of refinement.[11] Full-matrix refinement of the atomic positional and thermal parameters converged to final R and R' values of 0.0698 and 0.0613 respectively, with weights of $w = 1/\sigma^2 F_o$ assigned to the individual reflections. The phenyl groups were treated as rigid hexagons [d(C–C) = 1.395 Å, d(C–H) = 1.08 Å] with fixed thermal parameters of 0.08 Å^2 for the H atoms.

The final atomic co-ordinates are listed in Table 3. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom co-ordinates, and remaining bond distances and angles and intermolecular distances.

Acknowledgements

We thank the S.E.R.C. for a studentship (to T. A.), Johnson Matthey Ltd. for a generous loan of silver and ruthenium salts, and Mrs. L. J. Salter for drawing the diagrams.

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Received 26*th January* 1988; *Paper* 8/00371H