Cluster Chemistry. Part 45.[1] Synthesis and some Reactions of $[Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]^-$: *X*-Ray Crystal Structures of $[MRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)]$ (M = Cu, Ag, or Au)†

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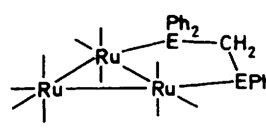
Reactions between $K[BHBu^s{}_3]$ and $[Ru_3(CO)_{10}(\mu\text{-}EPh_2CH_2EPh_2)]$ (E = P or As) afford solutions of the dephenylated anions, $[Ru_3(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9]^-$, which can be reversibly protonated to give $[Ru_3(\mu\text{-}H)(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9]$. The latter complexes may also be obtained directly from $[Ru_3(CO)_{10}(\mu\text{-}EPh_2CH_2EPh_2)]$ and H_2 (20 atm, 80 °C, 2 h) in cyclohexane (yields 65—75%). Similar complexes were obtained in poor yield from $[Ru_3(CO)_{10}(\mu\text{-}PPh_2CH_2CH_2PPh_2)]$. The group 1B metal-containing clusters $[MRu_3(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9(PPh_3)]$ (E = P, M = Cu, Ag, or Au; E = As, M = Au) were prepared from $[Ru_3(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9]^-$ and sources of $[M(PPh_3)]^+$; the analogous $[AuRu_3(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9(PPh_3)]$ was also obtained. Single-crystal *X*-ray studies on the first three, title complexes showed that they are isostructural, the $M(PPh_3)$ fragment bridging the same Ru–Ru bond as that bridged by the PPh group of the face-capping phosphido-phosphine ligand. Detailed examination of bond parameters in the Ru_2MP moiety suggests that the three $M(PPh_3)$ fragments are not strictly isolobal, although it is the $Ag(PPh_3)$ fragment which interacts least strongly with the Ru_3 core. The structures were refined by least-squares methods to residuals of 0.039, 0.044, and 0.041 for 4 560, 4 917, and 9 275 independent 'observed' reflections, respectively.

With the advent of mild synthetic routes to derivatives of $[Ru_3(CO)_{12}]$ containing tertiary phosphine, phosphite, and arsine ligands,[2] considerable interest in their chemistry has ensued. Extension of these studies to complexes containing bi- or tri-dentate ligands, in the hope that cluster degradation under more severe reaction conditions might be prevented, has uncovered an interesting microcosm of cluster chemistry. The thermal reaction between bis(diphenylphosphino)methane (dppm) and $[Ru_3(CO)_{12}]$ in tetrahydrofuran (thf) was first described in 1977,[3] when the fluxional properties of the resulting $[Ru_3(CO)_{10}(dppm)]$ (1) were also examined. A structural study of this molecule did not appear until seven years later, when the complex was obtained as one of the products of the reaction between $[Fe_2(CO)_9]$ and $[\{RuCl_2(p\text{-}MeC_6H_4CHMe_2)\}_2(dppm)]$ in refluxing benzene.[4] Meanwhile, the reaction between dppm and $[Ru_3(CO)_{12}]$ in xylene at 80—85 °C had been found to give $[Ru_3(CO)_8(dppm)_2]$ (2);[5] under more vigorous conditions, the complex $[Ru_3(\mu_3\text{-}PPh)(\mu_3\text{-}CHPPh_2)(CO)_7(dppm)]$ (3) is formed, and this complex may also be obtained by heating (2) in xylene at 100 °C. The present account describes an improved synthesis of (1), and its conversion to the anion $[Ru_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]^-$, together with some reactions of the latter. Some related studies of the arsine analogues are also included.

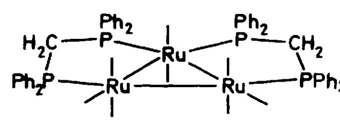
† μ_3-[(Diphenylphosphinomethyl)phenylphosphido-*P*(Ru[1],Ru[2]);-*P*′(Ru[3])]-1,2-μ-(triphenylphosphine)cuprio-*triangulo*-tris(tricarbonylruthenium), μ_3-[(diphenylphosphinomethyl)phenylphosphido-*P*(Ru[1],-Ru[2]);*P*′(Ru[3])]-1,2-μ-(triphenylphosphine)argentio-*triangulo*-tris(tricarbonylruthenium), and μ_3-[(diphenylphosphinomethyl)phenylphosphido-*P*(Ru[1],Ru[2]);*P*′(Ru[3])]-1,2-μ-(triphenylphosphine)aurio-*triangulo*-tris(tricarbonylruthenium) respectively.

Supplementary data available (No. SUP 56632, 17 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

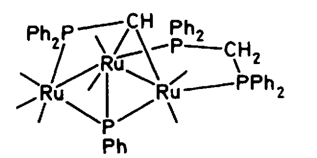
Non-S.I. units employed: eV ≈ 1.60×10^{-19} J, atm = 101 325 N m^{-2}.



(1) E = P
(4) E = As



(2)



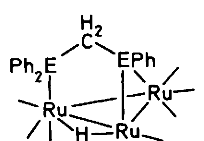
(3)

Results and Discussion

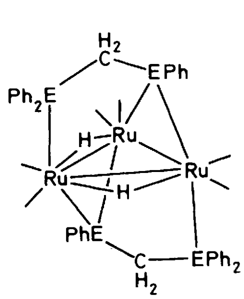
Following our earlier studies,[2] we have found that (1) can be obtained in 91% yield by the $Na[Ph_2CO]$-catalysed reaction between equimolar amounts of $[Ru_3(CO)_{12}]$ and dppm in warm thf. A similar yield reaction catalysed by $[N(PPh_3)_2][O_2CMe]$ has been reported recently.[6] An analogous reaction employing bis(diphenylarsino)methane (dpam) gave $[Ru_3(CO)_{10}(dpam)]$ (4) in 91% yield. Details of the reactions and characterisation of (1) and (4) are given in the Experimental section.

Treatment of (1) in thf solution with potassium selectride ($K[BHBu^s{}_3]$) at ambient temperature resulted in an immediate darkening, followed by a slow (hours) change in the colour of the solution from deep red to orange-yellow. The i.r. spectrum of this solution contained ν(CO) bands at 2 033 and 2 019 cm^{-1}. Protonation (H_3PO_4) and subsequent work-up afforded a monohydrido cluster which was readily identified as $[Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]$ (5) by elemental microanalysis and from its spectroscopic properties. Thus, the ^1H n.m.r. spectrum contained a high-field triplet (of relative intensity 1) at δ −16.65, assigned to a proton bridging a metal–metal bond, and a broad singlet (relative intensity 2) at δ 3.93 assigned to the CH_2 group. The aromatic multiplet at δ 7.44 had relative intensity 15 H, showing that one of the Ph groups of the dppm ligand originally present has been eliminated, probably as benzene, with concomitant formation of a μ-phosphido group. The arsenic analogue, (**6**), was obtained by a similar sequence of reactions, although the elimination of benzene occurs at a much slower rate than that found for (**1**).

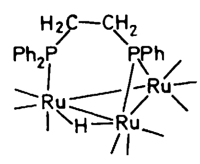
These unusual reactions probably proceed by initial formation of an anionic hydrido cluster, such as $[Ru_3H(CO)_9(dppm)]^-$ (Scheme). In support of this, the i.r. spectrum of the initial deep red solution contains a broad medium intensity absorption at 1 665 cm^{-1}, which is similar to that assigned to a ν(μ-CO) vibration in $[Ru_3H(CO)_{11}]^-$.[7] The subsequent elimination of benzene resembles well established reactions of other cluster hydrides containing tertiary phosphines or arsines, or thiolate ligands.[8] In most cases, however, cleavage of the



(**5**) E = P
(**6**) E = As



(**7**) E = P
(**8**) E = As



(**9**)

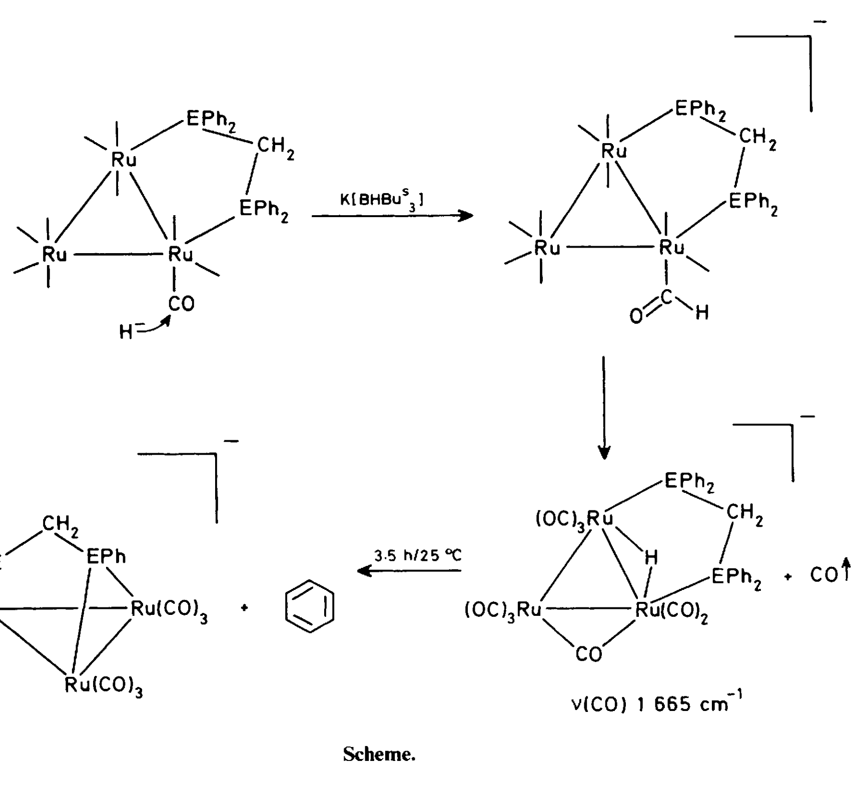
P–, As–, or S–carbon bond occurs on heating, and we believe that this is the first occasion on which such a process has been accomplished by addition of hydride ion. However, the formation of $[MnRu(\mu\text{-}PPh_2)(CO)_8(PPh_3)_2]$ in the reaction between $[RuCl_2(PPh_3)_3]$ and $[Mn(CO)_5]^-$ is assumed to proceed *via* an intermediate anionic hydrido complex.[9]

We note that deprotonation of the dppm or dpam ligands did not take place, probably because the approach of the bulky borate derivative to the methylene carbon is prevented by the phenyl groups.

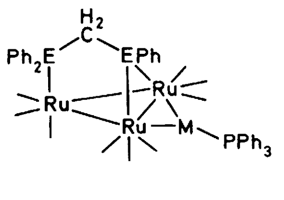
The formation of $[Ru_3H_2(\mu_3\text{-}EPhCH_2EPh_2)_2(CO)_6]$ (**7**, E = P; **8**, E = As), which are closely akin to (**5**) and (**6**), by hydrogenation of $[Ru_3(CO)_8(L\text{-}L)_2]$ (L–L = dppm or dpam, respectively),[10] provides earlier examples of the μ_3-phosphido-phosphine and μ_3-arsenido-arsine ligands. Indeed, complexes (**5**) and (**6**) may also be obtained similarly, by hydrogenation of (**1**) and (**4**) respectively under mild conditions (see Experimental section). Others have also reported the preparation of (**5**) by this route.[11]

Addition of $K[BHBu^s_3]$ to $[Ru_3(CO)_{10}(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane],[12] heating the mixture at reflux point overnight, and subsequent protonation, afforded $[Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9]$ (**9**) in low yield. The complex was identified by the usual methods [its spectroscopic properties were similar to those of (**5**)]; complex (**9**) was also obtained, in higher yield, together with $[Ru_4H_4(CO)_{10}(dppe)]$, by direct hydrogenation of $[Ru_3(CO)_{10}(dppe)]$.[13]

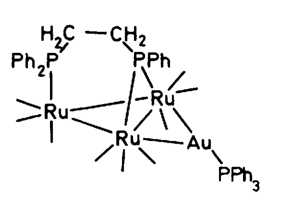
Reactions of the Anions $[Ru_3(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9]^-$ (E = P *or* As).—The anions generated from (**1**) or (**4**) by addition of $K[BHBu^s_3]$ proved to be useful synthetic intermediates. We have already described their use in the syntheses of aryldiazo[14] and allyl derivatives[15] of the cluster carbonyl. They also react readily with sources of $[M(PPh_3)]^+$ fragments (M = Cu, Ag, or Au) to give complexes in which the bridging hydride ligand in (**1**) or (**4**) has been replaced by the $M(PPh_3)$ group, a not unexpected result in view of the well established isolobal relationship between H and $Au(PPh_3)$.



Scheme.



(10) E = P, M = Cu
(11) E = P, M = Ag
(12) E = P, M = Au
(13) E = As, M = Au



(14)

Thus, when solutions of the anions were reacted with $[\{CuCl(PPh_3)\}_4]$, $[Ag\{C_5(CO_2Me)_5\}(PPh_3)]$,[16] or $[AuCl(PPh_3)]$, the colour changed slightly, and the orange to red crystalline complexes $[MRu_3(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9(PPh_3)]$ [E = P, M = Cu (**10**), Ag (**11**), or Au (**12**); E = As, M = Au (**13**)] were obtained in good yield. They were identified by elemental microanalyses and from their spectral characteristics. Their i.r. spectra contained well resolved ν(CO) patterns which resembled those of (**1**) or (**4**), while the ^1H n.m.r. spectra contained resonances from the bridging ligand and PPh_3, but no high-field signals as found in the parent hydrides. Unambiguous identification of all three complexes (**10**)—(**12**) was achieved by single-crystal *X*-ray diffraction studies, well formed crystals affording the opportunity to compare this series of Group 1B derivatives.

A similar reaction between the anion, generated by reaction of $K[BHBu^s{}_3]$ with $[Ru_3(CO)_{10}(dppe)]$, and $[AuCl(PPh_3)]$ gave the analogous complex $[AuRu_3(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9(PPh_3)]$ (**14**) as red crystals. This complex had generally similar i.r. ν(CO) spectra and ^1H n.m.r. spectra (except for the CH_2 resonances) to those of (**12**), and undoubtedly has a similar structure.

Crystal Structures of $[MRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)]$ (M = Cu, Ag, *or* Au).—Crystals of $[MRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)]$ [M = Cu (**10**), Ag (**11**), or Au (**12**)] are isomorphous and isostructural, the latter comment being qualified by the extent to which the structural similarity encompasses the resolved or unresolved disorder of some peripheral phenyl rings. The results of the structure determination are consistent with the above stoicheiometry and with a connectivity as depicted in the Figure for a molecule of (**12**). The four metal atoms are linked in a butterfly arrangement, with Ru(1,3) being bridged by the coinage metal. The same Ru–Ru vector is also bridged on the other side of the Ru_3 plane by the phosphido atom P(1) of the bidentate ligand. The latter is formed by loss of a phenyl group from P(1); one phenyl remains attached to this atom, which is also bonded to C(120) of the methylene group. The phosphido-phosphine is attached by P(2) to Ru(2) *via* a normal two-electron donor bond in an axial co-ordination position.

The following features of interest may be noted. (*i*) The symmetry of the MRu_3 core is quite a reasonable approximation to *m*; Ru(2)–Ru(1,3) are generally similar, but not equivalent. Ru(1)–Ru(2) lie in the range 2.891(2)—2.896(1) Å, while Ru(2)–Ru(3) are slightly shorter [2.867(2)—2.873(2) Å] (Table 1). In (**11**) and (**12**), Ru(1)–Ru(3) is much longer [2.944(1), 2.942(1) Å, respectively] than in (**10**) [2.885(1) Å]. The slight asymmetry in Ru(1,3)–Ru(2) is reflected in a similar and opposite asymmetry in M–Ru(1,3), the M–Ru(1) vector being generally *shorter* than the M–Ru(3) vector by 0.015—0.025 Å; this is also true of P(1)–Ru(1,3). The deviation of P(1) from the Ru(3) plane is substantially constant (Table 2) as is the dihedral angle of the associated $Ru_2P(1)$ plane; in contrast, the deviation of Cu from the Ru_3 plane is rather less than those of the Ag and Au atoms (which are almost identical). That this is not simply an effect of changing coinage metal radius alone is suggested by the change in the associated MRu_2/Ru_3 interplanar dihedral angles.

(*ii*) Within the co-ordination sphere of the MRu_3 core, the quasi-*m* symmetry suggested by the core is totally lost (Figure; Table 2); it would seem more reasonable to suppose that the relatively minor distortions of the core symmetry observed in (**10**) are a consequence of some more major perturbations in the latter, rather than the converse. A possible cause of abnormal distortion of the co-ordination sphere may arise from the bidentate ligand; the angle subtended at C(120) by the two phosphorus atoms is appreciably smaller than the tetrahedral norm. If P(1) and P(2) were to co-ordinate strictly at right angles to the Ru_3 plane, this value would be reduced even further; the resulting strain may explain the fact that atoms P(1)C(120)P(2) do not define a plane normal to Ru_3 but rather one in which C(120) is well removed from the edge of the tetrahedron, so that *m* symmetry is lost. In support of this, Ru(1,3)–Ru(2)–P(2) are noted as being unsymmetrical; C(22,23) lie out of the Ru_3 plane on the side opposite P(2), while Ru(1,3)–Ru(2)–C(21) are both well below 90°. In rebuttal of this argument, however, we note that CO(11,31), both lying above the Ru_3 plane on the side of C(120), have an asymmetry such that C(11) is much closer to C(120) than is C(31). Nevertheless,

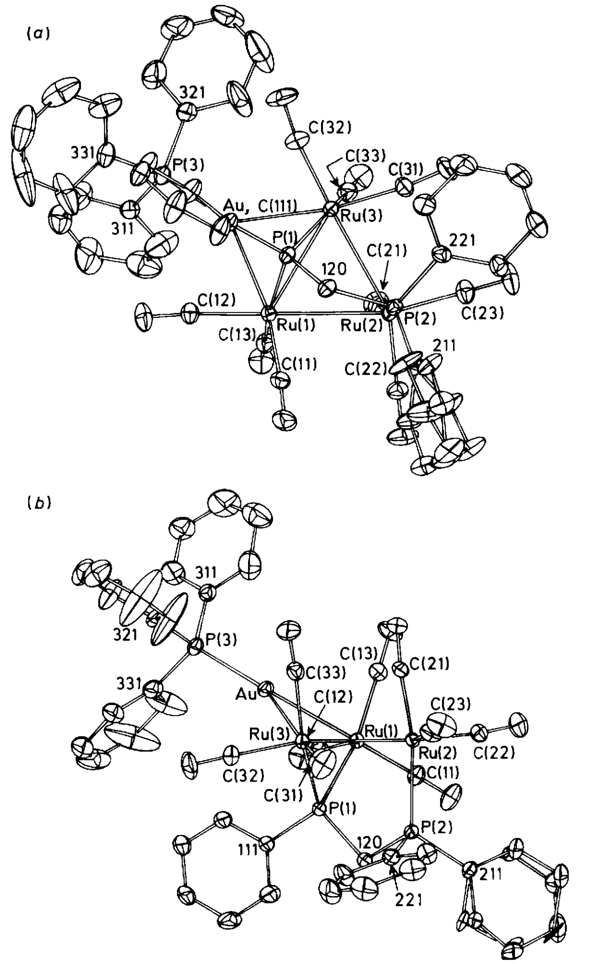


Figure. Projection of $[AuRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)]$ (**12**): (*a*) normal to and (*b*) through the Ru_3 plane. 20% Probability thermal ellipsoids are given for the non-hydrogen atoms, together with the basis of the numbering scheme. Phenyl ring 21 is disordered about its axis

Table 1. Metal and phosphorus atom environments. The first column in each matrix is the metal–ligand atom distance (Å); other entries are the angles (°) subtended by the atoms at the head of the relevant row and column. The geometry about the phosphorus atoms is given similarly

(*a*) Ru(1)

(10)	*r*	Ru(2)	Ru(3)	C(11)	C(12)	C(13)	P(1)
Cu	2.607(1)	109.56(3)	56.77(3)	164.8(2)	69.9(2)	80.9(2)	85.25(6)
Ru(2)	2.896(1)		59.61(3)	85.7(2)	174.1(2)	91.2(2)	78.33(5)
Ru(3)	2.885(1)			135.9(2)	117.0(2)	106.8(2)	51.99(5)
C(11)	1.889(8)				94.9(3)	99.7(3)	97.9(2)
C(12)	1.898(7)					94.5(3)	95.8(2)
C(13)	1.932(7)						158.8(2)
P(1)	2.316(2)						

(11)	*r*	Ru(2)	Ru(3)	C(11)	C(12)	C(13)	P(1)
Ag	2.767(1)	108.92(3)	58.75(3)	167.3(3)	73.2(2)	77.8(3)	87.80(7)
Ru(2)	2.894(1)		58.95(3)	83.5(3)	172.7(2)	92.0(2)	78.57(5)
Ru(3)	2.944(1)			133.0(3)	118.7(2)	108.1(2)	51.31(6)
C(11)	1.895(8)				94.8(4)	99.7(3)	97.4(3)
C(12)	1.888(9)					95.2(3)	94.7(2)
C(13)	1.939(8)						159.4(3)
P(1)	2.328(2)						

(12)	*r*	Ru(2)	Ru(3)	C(11)	C(12)	C(13)	P(1)
Au	2.751(1)	108.77(2)	58.49(2)	169.3(2)	74.5(2)	79.6(2)	87.53(5)
Ru(2)	2.891(1)		58.86(4)	81.8(2)	172.9(1)	92.6(2)	78.49(4)
Ru(3)	2.942(1)			131.3(2)	120.2(2)	109.8(2)	51.37(4)
C(11)	1.888(7)				95.2(3)	98.6(3)	96.6(2)
C(12)	1.897(6)					94.2(3)	95.5(2)
C(13)	1.928(6)						161.2(2)
P(1)	2.320(2)						

(*b*) Ru(2)

(10)	*r*	Ru(3)	C(21)	C(22)	C(23)	P(2)
Ru(1)	2.896(1)	60.00(2)	83.7(2)	94.2(3)	165.5(2)	92.74(6)
Ru(3)	2.873(1)		82.1(2)	153.7(3)	105.8(2)	89.86(6)
C(21)	1.897(7)			90.7(3)	91.5(3)	171.9(2)
C(22)	1.895(8)				99.6(4)	96.8(3)
C(23)	1.894(7)					90.3(2)
P(2)	2.415(2)					

(11)	*r*	Ru(3)	C(21)	C(22)	C(23)	P(2)
Ru(1)	2.894(1)	61.39(2)	82.0(3)	95.2(3)	163.7(3)	92.76(6)
Ru(3)	2.873(1)		80.9(2)	155.9(3)	103.1(3)	88.78(6)
C(21)	1.881(8)			90.7(4)	91.0(4)	169.7(2)
C(22)	1.904(8)				99.6(4)	98.7(3)
C(23)	1.888(9)					91.7(3)
P(2)	2.432(2)					

(12)	*r*	Ru(3)	C(21)	C(22)	C(23)	P(2)
Ru(1)	2.891(1)	61.45(2)	81.5(2)	95.5(2)	163.9(3)	92.89(5)
Ru(3)	2.867(1)		81.0(2)	156.5(2)	103.3(3)	88.60(5)
C(21)	1.875(6)			91.6(3)	91.4(3)	169.6(2)
C(22)	1.903(7)				99.1(3)	97.7(2)
C(23)	1.897(7)					91.8(2)
P(2)	2.419(2)					

(*c*) Ru(3)

(10)	*r*	Ru(1)	Ru(2)	C(31)	C(32)	C(33)	P(1)
Cu	2.622(1)	56.28(3)	109.82(3)	163.4(2)	78.7(3)	71.7(2)	84.52(6)
Ru(1)	2.885(1)		60.39(3)	135.9(2)	122.5(3)	102.4(2)	51.37(5)
Ru(2)	2.873(1)			77.1(2)	168.4(3)	96.3(2)	78.51(5)
C(31)	1.899(8)				96.9(4)	92.9(3)	111.9(4)
C(32)	1.844(9)					93.9(4)	94.9(3)
C(33)	1.916(8)						152.4(2)
P(1)	2.336(2)						

Table 1 (*continued*)

(*c*) Ru(3)

(11)	*r*	Ru(1)	Ru(2)	C(31)	C(32)	C(33)	P(1)
Ag	2.806(1)	57.48(4)	108.45(4)	162.2(3)	79.8(3)	72.8(3)	86.49(7)
Ru(1)	2.944(1)		59.67(4)	135.9(3)	122.5(3)	106.1(3)	50.66(6)
Ru(2)	2.873(2)			78.5(3)	168.8(3)	95.8(3)	78.70(6)
C(31)	1.886(9)				95.9(4)	90.4(4)	111.2(3)
C(32)	1.900(9)					94.0(4)	94.5(3)
C(33)	1.913(8)						155.8(3)
P(1)	2.349(2)						

(12)	*r*	Ru(1)	Ru(2)	C(31)	C(32)	C(33)	P(1)
Au	2.786(1)	57.33(3)	108.49(3)	163.3(2)	79.9(2)	74.3(2)	86.15(6)
Ru(1)	2.942(1)		59.69(4)	135.6(2)	122.7(2)	106.8(2)	50.51(4)
Ru(2)	2.867(2)			78.5(2)	168.7(2)	95.2(2)	78.57(5)
C(31)	1.887(7)				95.6(3)	90.2(3)	110.3(2)
C(32)	1.896(7)					94.5(3)	94.8(2)
C(33)	1.916(7)						156.5(2)
P(1)	2.348(2)						

(*d*) M [Cu (**10**), Ag (**11**), or Au (**12**)]

(10)	*r*	Ru(3)	P(3)
Ru(1)	2.607(1)	66.95(3)	149.13(7)
Ru(3)	2.622(1)		143.58(7)
P(3)	2.228(2)		

(11)	*r*	Ru(3)	P(3)
Ru(1)	2.767(1)	63.77(3)	151.76(7)
Ru(3)	2.806(1)		142.91(7)
P(3)	2.422(3)		

(12)	*r*	Ru(3)	P(3)
Ru(1)	2.751(1)	64.18(3)	151.47(6)
Ru(3)	2.786(1)		143.30(6)
P(3)	2.297(2)		

(*e*) P(1)

(10)	*r*	Ru(3)	C(111)	C(120)
Ru(1)	2.316(2)	76.64(6)	120.8(2)	114.0(2)
Ru(3)	2.336(2)		121.1(2)	123.7(2)
C(111)	1.830(7)			100.8(3)
C(120)	1.850(7)			

(11)	*r*	Ru(3)	C(111)	C(120)
Ru(1)	2.328(2)	78.03(7)	119.1(3)	113.8(3)
Ru(3)	2.349(2)		120.9(3)	122.3(3)
C(111)	1.827(8)			102.3(3)
C(120)	1.852(8)			

(12)	*r*	Ru(3)	C(111)	C(120)
Ru(1)	2.320(2)	78.12(5)	119.3(2)	113.8(2)
Ru(3)	2.348(2)		120.6(2)	122.3(2)
C(111)	1.840(6)			102.4(3)
C(120)	1.842(6)			

(*f*) P(2)

(10)	*r*	C(120)	C(211)	C(221)
Ru(2)	2.415(2)	112.0(2)	118.9(2)	116.0(2)
C(120)	1.814(8)		104.4(3)	102.6(3)
C(211)	1.833(7)			101.0(3)
C(221)	1.823(8)			

(11)	*r*	C(120)	C(211)	C(221)
Ru(2)	2.432(2)	111.7(3)	121.4(3)	114.2(3)
C(120)	1.826(8)		102.8(4)	104.5(4)
C(211)	1.834(8)			100.3(3)
C(221)	1.841(9)			

(12)	*r*	C(120)	C(211)	C(221)
Ru(2)	2.419(2)	111.7(2)	121.4(2)	115.4(2)
C(120)	1.825(6)		102.9(3)	102.9(3)
C(211)	1.830(6)			100.3(3)
C(221)	1.830(6)			

(*g*) P(3)

(10)	*r*	C(311)	C(321)	C(331)
Cu	2.228(2)	117.0(3)	113.3(2)	112.6(3)
C(311)	1.812(7)		102.4(3)	105.5(4)
C(321)	1.820(8)			104.8(4)
C(331)	1.813(8)			

(11)	*r*	C(311)	C(321)	C(331)
Ag	2.422(3)	118.5(3)	112.6(3)	111.4(3)
C(311)	1.804(8)		102.5(4)	105.0(4)
C(321)	1.835(9)			105.7(4)
C(331)	1.827(10)			

(12)	*r*	C(311)	C(321)	C(331)
Au	2.297(2)	117.4(2)	113.3(2)	111.4(3)
C(311)	1.805(6)		102.5(3)	106.3(3)
C(321)	1.815(7)			104.7(3)
C(331)	1.821(7)			

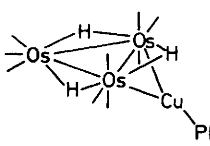
P(1)–C(120)–P(2) are 105.8(3), 105.8(4), 105.6(3)° for (**10**), (**11**), and (**12**) respectively.

methylene-bridged chelating tertiary phosphine ligands have a history of unusual steric behaviour, *e.g.* in [$PdCl_2$(dppm)], the angle P–Pd–P is closed down to 73.3°, with a P–C–P angle of only 93.0° and Pd–P–C angles of 94.7 and 94.3°, the C atom lying out of the PdP_2 plane by 0.50 Å; the *trans* Cl atoms in the 'square planar' co-ordination sphere are also deviant by −0.18 and 0.30 Å.[17]

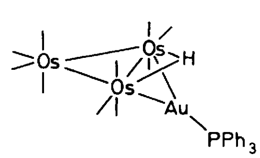
(*iii*) Also of comparative interest are the related osmium cluster compounds, [$CuOs_3(\mu\text{-}H)_3(CO)_9(PPh_3)$] (**15**)[18] and [$AuOs_3(\mu\text{-}H)(CO)_{10}(PPh_3)$] (**16**).[19] In the former, the Cu–Os distances [2.695(5) and 2.726(5) Å] are appreciably *longer* than in the present complex (**10**); the $Os_3/CuOs_2$ interplanar dihedral angle is very different [72.2 *vs.* 46.4° in (**10**)]. The Cu–P distance [2.213(8) Å] does not differ significantly from that found in

Table 2. Ru_3 planes. Atom deviations, δ, from the Ru_3 planes are tabulated in Å; θ° is the associated MRu_2 dihedral angle and φ° the P(1) Ru_2 dihedral angle

	Cu	Ag	Au
δM	1.155	1.394	1.371
δP(1)	−1.801	−1.785	−1.781
δC(11)	−0.897	−0.929	−0.933
δC(12)	−0.161	−0.229	−0.233
δC(13)	1.828	1.821	1.790
δP(2)	−2.411	−2.426	−2.412
δC(21)	1.876	1.852	1.846
δC(22)	0.174	0.201	0.160
δC(23)	0.110	0.169	0.178
δC(31)	−0.391	−0.465	−0.495
δC(32)	−0.353	−0.358	−0.359
δC(33)	1.871	1.835	1.830
θ	46.4	36.1	35.8
φ	80.8	79.3	79.4



(15)



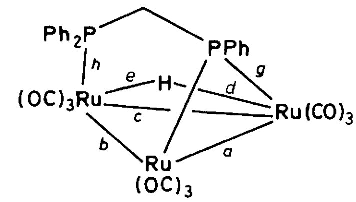
(16)

(10). In (16), on the other hand, the Au–Os distances [2.772(2) and 2.738(1) Å] are similar to those in (12), while the Au–P distance of 2.320(7) Å in (16) is slightly longer than in the present complex. The interplanar dihedral angle (70.2°) is similar to that in (15), but again different from that in (12) (35.8°). No comparable study exists of a silver derivative; this is unfortunate, since one of the most interesting results of the present work is the very long Ag–P distance [2.422(3) Å], compared with the Cu–P and Au–P values [2.228(2) and 2.297(2) Å, respectively].

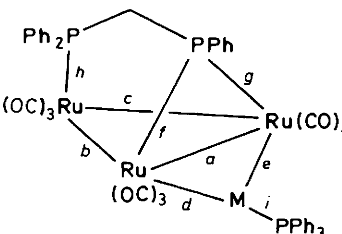
This study is the first comparison available of the geometries of the three coinage metals occupying similar bridging sites in a metal cluster, and is of interest particularly in the context of the isolobal relationship between the $M(PPh_3)$ groups and the H atom, first pointed out in 1981,[20] and also of the extended discussion of the relationships between the three coinage metals. It is fortunate that the molecular structure of the isolobal complex $[Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2PPh_2)(CO)_9]$ (5) has also been reported.[12] Table 3 includes selected structural parameters for this complex as well. There is a major difference between the solid-state structure of (5) and those described above, namely, that the H atom is bridging Ru(1)–Ru(2), and is coplanar with the Ru_3 atoms. In solution, the H bridge is fluxional. We have previously described the structure of $[AuFe_3(\mu_3\text{-}\eta^2\text{-HC=NBu}^t)(CO)_9(PPh_3)]$, in which the $Au(PPh_3)$ group bridges a different Fe–Fe vector from that bridged by the H in $[Fe_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-HC=NBu}^t)(CO)_9]$;[21] again, however, the H bridge is fluxional in solution, and the structure adopted in the solid state is determined by crystal-packing considerations.

In developing their discussion on the differences in bonding modes of the Group 1B $M(PPh_3)$ fragments, Evans and Mingos[22] suggested that the degenerate p_x and p_y orbitals of gold are of relative high energy, compared with those of copper. In a capping situation, the frontier molecular orbitals for $Cu(PPh_3)$ are likely to involve these two π-type orbitals and the hybrid(s–z) orbital, whereas for $Au(PPh_3)$, only the latter will be important in bonding. Previous comparisons between these Group 1B metals have involved the Cu(NCMe) and $Au(PR_3)$ fragments, for example, in the carbido complexes $[M_2Ru_6C(CO)_{16}(L)_2]$ (M = Au, L = $PMePh_2$;[23a] M = Cu, L = MeCN[23b]) and $[MOs_{10}C(CO)_{24}(L)]$[24] (M = Cu, L = MeCN; M = Au, L = PPh_3), in which some geometrical differences were ascribed to differences in bonding. Studies of the hexanuclear clusters $[MM'Ru_4(\mu_3\text{-H})(CO)_{12}(PPh_3)_2]$ (M,M′ = Cu, Ag, or Au) have concluded that the lighter Group 1B element occupied the site of highest co-ordination number;[25] in the examples of $[MCo_3Ru(CO)_{12}(PPh_3)]$ (17) (M = Cu and Au), in which the $M(PPh_3)$ fragment caps a Co_3 face on the opposite side to the $Ru(CO)_3$ group, no differences were found for the M–Co bond lengths other than those arising from differences in covalent radii.[26] An extended-Hückel molecular orbital calculation carried out by these authors suggests that the p_x and p_y levels in the $Cu(PH_3)$ and $Au(PH_3)$ fragments do not differ significantly (−6.33 *vs.* −5.93 eV). Finally, we refer to the anionic complexes $[M\{Os_3H(CO)_{10}\}_2]^-$ (M = Ag[27] or Au[28]) in which the Os–Ag distances [2.852(1)—2.874(1) Å] are also *ca.* 0.06 Å *longer* than the corresponding Os–Au distances [2.802(1)—2.814(1) Å].

Table 3. Selected bond parameters for complexes $[Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2PPh_2)(CO)_9]$ (5) and $[MRu_3(\mu_3\text{-PPhCH}_2PPh_2)(CO)_9(PPh_3)]$ [M = Cu (10), Ag (11), or Au (12)]



(5)

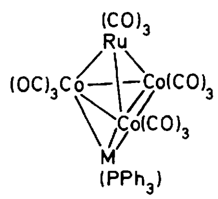


(10) - (12)

	Complex			
	(5)*	(10)	(11)	(12)
(*i*) Bond distances/Å				
a	2.820(1)	2.885(1)	2.944(1)	2.942(1)
b	2.890(1)	2.873(1)	2.873(1)	2.867(1)
c	3.012(1)†	2.896(1)	2.894(1)	2.891(1)
d	1.815(32)	2.622(1)	2.806(1)	2.786(1)
e	1.827(32)	2.607(1)	2.767(1)	2.751(1)
f	2.306(1)	2.336(2)	2.349(2)	2.348(2)
g	2.332(1)	2.316(2)	2.328(2)	2.320(2)
h	2.384(1)	2.415(2)	2.432(2)	2.419(2)
i		2.228(2)	2.422(3)	2.297(2)
(*ii*) Dihedral angles/°				
Ru_3/Ru_2M		46.4(1)	36.1(1)	35.8(1)
Ru_3/Ru_2P	83.8(1)	80.8(1)	81.5(1)	79.4(1)

* Ref. 12. † Bridged by H.

Returning to the structures of complexes (10), (11), and (12), we find that, within the $PMRu_3$ core, changes in bond lengths along the series M = Cu, Ag, Au suggest that the $Cu(PPh_3)$ moiety is the most tightly held (shortest M–Ru, Ru–Ru distances in $CuRu_2$ triangle) and that the silver derivative may be the exception (longest M–Ru, M–P distances). It is interesting to note that within the Group 1B metals themselves, the Ag–Ag bond strength is anomalously low when compared with copper and gold and a connection can be traced to the weaker Ag–H bond compared with CuH and AuH.[29] Alternatively, the edge-bridging $M(PPh_3)$ units in these complexes may utilise the hybrid(*s*–*z*) orbital and one of the degenerate p_x and p_y orbitals in the copper and silver examples, but only the former in the gold complex, a closer approach of the $Au(PPh_3)$ affording a better overlap with the appropriate edge orbitals of the Ru_3 cluster. While our results can be interpreted as giving qualitative support to a view that the three $M(PPh_3)$ groups are isolobal in edge-bridging as well as face-capping positions, further comparative studies, particularly of silver-containing complexes, are required to quantify the position of these Group 1B metal fragments.



(17) M = Cu or Au

Experimental

General experimental conditions are similar to those described in other papers from this Laboratory. All reactions were carried out under nitrogen, but no special precuations to exclude air were taken during work-up. $[Ru_3(CO)_{12}]$ was made by a literature method;[30] the ligands dppm, dpam, and dppe were obtained from Strem Chemical Co., Newburyport, Massachusetts, and used as received. ^{31}P Chemical shifts were referenced to external H_3PO_4 (85% aqueous solution).

Preparation of $[Ru_3(CO)_{10}(dppm)]$ (**1**).—A mixture of $[Ru_3(CO)_{12}]$ (1.0 g, 1.56 mmol) and dppm (0.62 g, 1.61 mmol) in thf (100 cm^3) was warmed to 40 °C to dissolve all of the carbonyl. A solution of $Na[Ph_2CO]$ in thf (*ca.* 0.025 mol dm^{-3}) was added dropwise from a syringe until the solution darkened and the 2 061 cm^{-1} band of $[Ru_3(CO)_{12}]$ was absent (1—5 drops). The solution volume was reduced to *ca.* 5 cm^3 (rotary evaporator). Addition of MeOH (40 cm^3) and cooling gave orange-red crystals of $[Ru_3(CO)_{10}(dppm)]$ (**1**) (1.37 g, 91%), m.p. 180—181 °C (Found: C, 43.75; H, 2.05. $C_{35}H_{22}O_{10}P_2Ru_3$ requires C, 43.45; H, 2.30%). I.r. (cyclohexane): ν(CO) at 2 086m, 2 024 (sh), 2 018s, 2 005s, 1 991w, 1 968m, 1 965m, and 1 947w cm^{-1} [lit.,[3] ν(CO) (CH_2Cl_2) at 2 080m, 2 040w, 2 010s, 1 988 (sh), and 1 960m cm^{-1}]. ^1H N.m.r. ($CDCl_3$): δ, 4.29 [t, *J*(HP) 10.5 Hz, 2 H, CH_2] and 7.37 (m, 20 H, Ph).

Preparation of $[Ru_3(CO)_{10}(dpam)]$ (**4**).—This complex was obtained in 91% yield by the $Na[Ph_2CO]$-catalysed reaction between $[Ru_3(CO)_{12}]$ and dpam, carried out as described above for the dppm complex, m.p. 170—174 °C (Found: C, 39.80; H, 1.95. $C_{35}H_{22}As_2O_{10}Ru_3$ requires C, 39.80; H, 2.10%). I.r. (cyclohexane): ν(CO) at 2 087m, 2 028w, 2 014vs, 2 010 (sh), 1 993w, 1 968m, and 1 962m cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ, 4.15 (s, 2 H, CH_2) and 7.38 (m, 20 H, Ph).

Preparation of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]$ (**5**).—A solution of $[Ru_3(CO)_{10}(dppm)]$ (150 mg, 0.155 mmol) in thf (10 cm^3) was treated with $K[BHBu^s{}_3]$ (0.31 cm^3 of a 0.5 mol dm^{-3} solution in thf, 0.155 mmol). An immediate darkening in colour to deep red occurred initially, followed by a gradual lightening to orange after stirring at 25 °C for 5 h. Addition of H_3PO_4 (0.25 cm^3) to the reaction mixture resulted in a further lightening in colour to yellow. The solvent was evaporated and the residue extracted with light petroleum (b.p. range 40–60 °C) (3 × 10 cm^3). The combined filtered extracts were taken to dryness, crystallisation from Et_2O–MeOH affording yellow crystals of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]$ (**5**) (92 mg, 69%), m.p. 135—140 °C (decomp.) [Found: C, 38.85; H, 1.65%; *M* (mass spectrum), 865. $C_{28}H_{18}O_9P_2Ru_3$ requires C, 38.95; H, 2.10%; *M*, 865]. I.r. (cyclohexane): ν(CO) at 2 084s, 2 053vs, 2 031vs, 2 014m, 2 001m, 1 996m, 1 990m, 1 984m, and 1 964w cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ, −16.65 [t, br, *J*(HP) 10.8 Hz, 1 H, RuH], 3.93 (s br, 2 H, CH_2), and 7.44 (m, 15 H, Ph).

Attempts to isolate the first-formed deep red anion, for example, by crystallisation with $[N(PPh_3)_2]Cl$, were not successful. The i.r. spectrum contains a ν(CO) band at 1 665m cm^{-1}, which is characteristic of a μ-CO ligand in anionic hydrido clusters.

Preparation of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}AsPhCH_2AsPh_2)(CO)_9]$ (**6**).—A solution of $[Ru_3(CO)_{10}(dpam)]$ (100 mg, 0.095 mmol) in thf (10 cm^3) was treated with $K[BHBu^s{}_3]$ (0.2 cm^3 of a 0.5 mol dm^{-3} solution in thf, 0.10 mmol). After stirring at 25 °C for 20 h H_3PO_4 (0.25 cm^3) was added. The solution was then taken to dryness and the residue extracted with light petroleum (3 × 10 cm^3). The combined filtered extracts were taken to dryness, crystallisation from Et_2O–MeOH affording orange-yellow crystals of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}AsPhCH_2AsPh_2)(CO)_9]$ (**6**) (48 mg, 53%), m.p. 157—159 °C (decomp.) (Found: C, 35.75; H, 1.65. $C_{28}H_{18}As_2O_9Ru_3$ requires C, 35.35; H, 1.90%). I.r. (cyclohexane): ν(CO) at 2 081s, 2 052vs, 2 029vs, 2 009s, 1 992s, 1 979w, and 1 968m cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ, −16.35 (s br, 1 H, RuH), 4.47 (s br, 2 H, CH_2), and 7.45 (m, 15 H, Ph). ^{13}C N.m.r. ($CDCl_3$): δ, 41.93 (s br, CH_2), 128.93—142.98 (m, Ph), and 196.46 (s br, CO).

Preparation of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9]$ (**9**).—A solution of $[Ru_3(CO)_{10}(dppe)]$ (100 mg, 0.102 mmol) in thf (10 cm^3) was treated with $K[BHBu^s{}_3]$ (0.22 cm^3 of a 0.5 mol dm^{-3} solution in thf, 0.11 mmol). After stirring at reflux for 18 h H_3PO_4 (0.25 cm^3) was added. The solution was taken to dryness and the residue extracted with light petroleum (3 × 10 cm^3). The combined yellow filtered extracts were taken to dryness; crystallisation from CH_2Cl_2–MeOH gave an orange-yellow powder of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9]$ (**9**) (22 mg, 25%).

This complex was identified by comparison of its ν(CO) spectrum with that of a sample prepared as described below.

Only $[Ru_3(CO)_{10}(dppe)]$ was recovered (70%) after stirring with $K[BHBu^s{}_3]$ at room temperature for 5 h, followed by addition of H_3PO_4.

Hydrogenation of $[Ru_3(CO)_{10}(L\text{–}L)]$ (L–L = dppm *or* dpam).—A solution of $[Ru_3(CO)_{10}(dppm)]$ (200 mg, 0.206 mmol) in cyclohexane (40 cm^3) was heated in an autoclave (80 °C, 2 h) under H_2 (20 atm). The resulting yellow solution was filtered and evaporated to dryness. Crystallisation of the residue (Et_2O–MeOH) gave yellow crystals of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9]$ (**5**) (134 mg, 75%), identified by comparison of its i.r. spectrum with an authentic sample.

A similar reaction of $[Ru_3(CO)_{10}(dpam)]$ afforded orange-yellow crystals (from Et_2O–MeOH) of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}AsPhCH_2AsPh_2)(CO)_9]$ (**6**) (117 mg, 65%), identified by comparison with an authentic sample (i.r.).

Hydrogenation of $[Ru_3(CO)_{10}(dppe)]$.—A solution of $[Ru_3(CO)_{10}(dppe)]$ (200 mg, 0.204 mmol) in cyclohexane (40 cm^3) was heated in an autoclave (80 °C, 5 h) under H_2 (25 atm). The resulting yellow solution was taken to dryness and separated by preparative t.l.c. [light petroleum–acetone (90:10)] to give 4 bands. Band 1, R_f 0.36, yellow, crystallised (CH_2Cl_2–MeOH) to give an orange powder of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9]$ **(9)** (60 mg, 34%), m.p. 110—115 °C [Found: C, 39.85; H, 2.30%; *M* (mass spectrum), 879. $C_{29}H_{20}O_9P_2Ru_3$ requires C, 39.70; H, 2.30%, *M*, 879]. I.r. (cyclohexane): ν(CO) at 2 087m, 2 043s, 2 016vs, 2 007w, 1 995w, 1 990w, 1 979m, and 1 968w cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ, −16.36 (s br, 1 H, RuH), 4.46 (s br, 4 H, CH_2), and 7.45 (m, 15 H, Ph). Band 4, R_f 0.13, yellow, crystallised (CH_2Cl_2–MeOH) to give orange crystals of $[Ru_4H_4(CO)_{10}(dppe)]$ (52 mg, 23%) identified by comparison of i.r. and ^1H n.m.r. data with literature values.[1,2] Bands 2 and 3 were obtained in trace amounts and were not identified.

Preparation of Group 1B *Derivatives.*—(*a*) $[CuRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)]$ **(10)**. A solution of $[Ru_3(CO)_{10}(dppm)]$ (300 mg, 0.309 mmol) in thf (10 cm^3) was treated with $K[BHBu^s_3]$ (0.63 cm^3 of a 0.5 mol dm^{-3} solution in thf, 0.315 mmol). After stirring at 25 °C for 5 h, the initial deep red solution had lightened to orange. Solid $[\{CuCl(PPh_3)\}_4]$ (114 mg, 0.315 mmol) was added to the anionic solution resulting in a further change in colour to a deeper orange. After stirring at ambient temperature for 30 min solvent was removed and the residue extracted with diethyl ether (3 × 20 cm^3). Filtration through Celite, addition of methanol (30 cm^3) to the filtrate, and reduction of the solution volume to *ca.* 10 cm^3 gave $[CuRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)]$ **(10)** as an orange powder (297 mg, 81%), m.p. 179—184 °C (decomp.) (Found: C, 46.25; H, 2.85. $C_{46}H_{32}CuO_9P_3Ru_3$ requires C, 46.50; H, 2.70%). I.r. (cyclohexane): ν(CO) at 2 057m, 2 013vs, 2 007 (sh), 1 996m, 1 984w, 1 965m, and 1 947m cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ, 4.38 [dd, *J*(PH) 10.0, 12.2 Hz, 2 H, CH_2] and 7.39 (m, 30 H, Ph).

(*b*) $[AgRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)]$ **(11)**. The cluster anion was prepared by the above method using $[Ru_3(CO)_{10}(dppm)]$ (100 mg, 0.103 mmol), thf (10 cm^3), and $K[BHBu^s_3]$ (0.21 cm^3 of a 0.5 mol dm^{-3} solution in thf, 0.105 mmol). A solution of $[Ag\{C_5(CO_2Me)_5\}(PPh_3)]$ (75 mg, 0.103 mmol) in thf (50 cm^3) was added dropwise (0.5 h) to the anionic solution, resulting in a darkening from orange to red. After removal of the solvent, the residue was extracted with CH_2Cl_2 (2 × 10 cm^3) and filtered through Celite. Addition of MeOH (20 cm^3) to the filtrate followed by concentration to *ca.* 20 cm^3 (rotary evaporator) and cooling to 0 °C gave well formed deep red crystals of $[AgRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)]$ **(11)** (104 mg, 82%), m.p. 198—201 °C (Found: C, 44.35; H, 2.25. $C_{46}H_{32}AgO_9P_3Ru_3$ requires C, 44.80; H, 2.60%). I.r. (cyclohexane): ν(CO) at 2 054m, 2 014vs, 2 000s (sh), 1 985m, 1 961w, and 1 950m cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ, 4.54 [dd, *J*(PH) 9.5, 11.7 Hz, 2 H, CH_2] and 7.45 (m, 30 H, Ph).

(*c*) $[AuRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)]$ **(12)**. A solution of $[Ru_3(CO)_{10}(dppm)]$ (100 mg, 0.103 mmol) in dry thf (10 cm^3) was treated with $K[BHBu^s_3]$ (0.21 cm^3 of a 0.5 mol dm^{-3} solution in thf, 0.105 mmol). After stirring at 25 °C for 5 h, the initial deep red solution lightened to orange. Solid $[AuCl(PPh_3)]$ (52 mg, 0.105 mmol) was added and the mixture stirred for 30 min. The solution was taken to dryness, extracted with diethyl ether (3 × 25 cm^3), and filtered through Celite. Evaporation and recrystallisation (CH_2Cl_2–MeOH) afforded orange-red crystals of $[AuRu_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_9(PPh_3)]$ **(12)** (100 mg, 74%), m.p. 224—226 °C (decomp.) (Found: C, 41.55; H, 2.10. $C_{46}H_{32}AuO_9P_3Ru_3$ requires C, 41.80; H, 2.45%). I.r. (cyclohexane): ν(CO) at 2 058m, 2 023vs, 2 011s, 1 992m, 1 977w, and 1 963m cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ, 4.62 [dd, *J*(PH) 10.0, 12.4 Hz, 2 H, CH_2] 7.43 (m, 30 H, Ph). ^{13}C N.m.r. ($CDCl_3$): δ, 45.33 [dd, *J*(PC) 19.1, 26.5 Hz, CH_2], 127.8—146.6 (m, Ph), and 198.7—199.9 (CO). ^{31}P N.m.r. ($CDCl_3$): δ, 11.46 [d, *J*(PP) 117, PPh_2], 68.68 (s, PPh_3), and 128.81 [d, *J*(PP) 117 Hz, PPh].

(*d*) $[AuRu_3(\mu_3\text{-}AsPhCH_2AsPh_2)(CO)_9(PPh_3)]$ **(13)**. A reaction similar to (*c*), using $[Ru_3(CO)_{10}(dpam)]$ (100 mg, 0.095 mmol), gave large well formed crystals of $[AuRu_3(\mu_3\text{-}AsPhCH_2AsPh_2)(CO)_9(PPh_3)]$ **(13)** (101 mg, 75%), m.p. 191—195 °C (Found: C, 39.10; H, 2.00. $C_{46}H_{32}As_2AuPRu_3$ requires C, 39.20; H, 2.30%). I.r. (cyclohexane): ν(CO) at 2 070vw, 2 056m, 2 040vw, 2 022vs, 2 009s, 1 989m, 1 974w, 1 965m, and 1 960w cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ, 4.46 (s, 2 H, CH_2) and 7.43 (m, 30 H, Ph).

(*e*) $[AuRu_3(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9(PPh_3)]$ **(14)**. A solution of $[Ru_3(CO)_{10}(dppe)]$ (50 mg, 0.051 mmol) in dry thf (10 cm^3) was treated with $K[BHBu^s_3]$ (0.15 cm^3 of a 0.5 mol dm^{-3} solution in thf, 0.08 mmol). After stirring at 40 °C for 5 h, solid $[AuCl(PPh_3)]$ (28 mg, 0.057 mmol) was added and the mixture stirred for 2 h. The solution was extracted with diethyl ether (3 × 10 cm^3) and filtered. Evaporation and crystallisation from CH_2Cl_2–isopentane afforded red crystals of $[AuRu_3(\mu_3\text{-}PPhCH_2CH_2PPh_2)(CO)_9(PPh_3)]$ **(14)** (18 mg, 26%), m.p. 206—209 °C (Found: C, 42.15; H, 2.45. $C_{47}H_{34}AuO_9P_3Ru_3$ requires C, 42.25; H, 2.55%). I.r. (cyclohexane): ν(CO) at 2 073m, 2 021s, 2 009m, 1 997vs, 1 991w, 1 969w, 1 950m, and 1 936w cm^{-1}. ^1H N.m.r. ($CDCl_3$): δ, 4.45 (s br, 4 H, CH_2) and 7.45 (m, 30 H, Ph).

Crystallography.—Unique data sets were measured at 295 K within preset $2\theta_{max.}$ limits using a Syntex $P2_1$ four-circle diffractometer in conventional 2θ/θ scan mode and fitted with a monochromatic Mo-K_α radiation source (λ = 0.710 6₉ Å). *N* Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the basically 9 × 9 block-diagonal least-squares refinement after Gaussian absorption correction and solution of the structure by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms (exception: some disordered ring components); $(x,y,z,U)_H$ were included as constrained estimates. Residuals quoted at convergence are R,R' (on $|F|$), reflection weights being statistical. Neutral complex scattering factors were used;[31] computation used the XTAL 83 program system[32] implemented on a Perkin-Elmer 3240 by S. R. Hall. Atom labelling is shown in the molecular projections. The three complexes are isostructural, except perhaps in respect of some disordered phenyl ring components, this being confined to one ring only in **(11)** and **(12)** and much more widespread in **(10)**; in **(11)** and **(12)**, however, high thermal motion in some rings may be a foil for disorder.

Crystal Data.—*For* **(10)**. $C_{46}H_{32}CuO_9P_3Ru_3$, *M* = 1 188.4, monoclinic, space group $P2_1/n$ (variant of C^5_{2h}, no. 14), *a* = 17.345(5), *b* = 22.533(8), *c* = 11.995(4) Å, β = 91.19(2)°, *U* = 4 687(3) Å^3, D_m = 1.68(1), D_c (*Z* = 4) = 1.69 g cm^{-3}, *F*(000) = 2 344, μ_{Mo} = 15.3 cm^{-1}. Specimen: 0.18 × 0.12 × 0.30 mm. $2\theta_{max.}$ = 50°, *N* = 7 586, N_o = 4 560. *R* = 0.039, *R′* = 0.034.

For **(11)**. $C_{46}H_{32}AgO_9P_3Ru_3$, *M* = 1 232.8, monoclinic, space group $P2_1/n$, *a* = 17.009(9), *b* = 22.694(10), *c* = 12.306(5) Å, β = 91.51(4)°, *U* = 4 749(4) Å^3, D_m = 1.73(1), D_c (*Z* = 4) = 1.87 g cm^{-3}, *F*(000) = 2 544, μ_{Mo} = 42.6 cm^{-1}. Specimen: 0.10 × 0.10 × 0.35 mm. $2\theta_{max.}$ = 50°, *N* = 8 378, N_o = 4 917. *R* = 0.044, *R′* = 0.035.

For **(12)**. $C_{46}H_{32}AuO_9P_3Ru_3$, *M* = 1 322.0, monoclinic, space group $P2_1/n$, *a* = 17.036(9), *b* = 22.556(12), *c* = 12.238(6) Å, β = 91.45(3)°, *U* = 4 701(4) Å^3, D_m = 1.86(1), D_c (*Z* = 4) = 1.87 g cm^{-3}, *F*(000) = 2 544, μ_{Mo} = 42.6 cm^{-1}. Specimen: 0.50 × 0.27 × 0.58 mm. $2\theta_{max.}$ = 65°, *N* = 17 140, N_o = 9 275. *R* = 0.041, *R′* = 0.049.

Carbonyl geometries are given in Table 4 and atomic coordinates in Table 5.

Table 4. Carbonyl geometries

	Distance r_{C-O}/Å			Angle Ru–C–O/°		
Carbonyl	**(10)**	**(11)**	**(12)**	**(10)**	**(11)**	**(12)**
11	1.146(10)	1.150(10)	1.138(9)	178.7(7)	178.0(8)	176.2(6)
12	1.136(9)	1.158(10)	1.140(8)	172.8(7)	174.2(7)	174.5(6)
13	1.137(9)	1.145(10)	1.145(8)	176.0(6)	176.2(7)	177.7(6)
21	1.146(9)	1.162(10)	1.151(7)	173.4(6)	172.5(7)	172.9(6)
22	1.138(10)	1.137(10)	1.138(8)	175.1(7)	176.2(8)	174.6(6)
23	1.132(9)	1.149(11)	1.137(8)	176.3(6)	175.2(8)	175.0(7)
31	1.127(10)	1.148(12)	1.133(9)	171.4(7)	170.4(8)	169.0(6)
32	1.164(12)	1.124(11)	1.133(9)	174.7(8)	173.5(9)	173.2(7)
33	1.148(10)	1.152(11)	1.147(9)	174.9(7)	174.5(7)	174.5(6)

Table 5. Non-hydrogen atomic co-ordinates

	(10) M = Cu			**(11)** M = Ag			**(12)** M = Au		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
M	0.270 00(6)	0.431 83(4)	0.656 28(7)	0.272 58(4)	0.434 01(3)	0.657 82(5)	0.269 10(2)	0.434 75(1)	0.660 70(2)
Ru(1)	0.367 79(3)	0.422 85(2)	0.494 98(5)	0.372 62(4)	0.425 90(3)	0.484 74(5)	0.370 59(3)	0.426 54(2)	0.490 04(3)
Ru(2)	0.387 15(3)	0.299 13(3)	0.436 55(5)	0.389 00(4)	0.303 22(3)	0.425 16(5)	0.387 43(3)	0.303 12(2)	0.431 34(3)
Ru(3)	0.244 64(3)	0.339 12(3)	0.528 57(5)	0.242 07(4)	0.342 24(3)	0.509 84(5)	0.240 32(3)	0.342 32(2)	0.514 08(3)
Carbonyl groups									
C(11)	0.438 7(4)	0.438 5(3)	0.381 2(6)	0.446 0(5)	0.438 0(4)	0.373 7(6)	0.443 9(4)	0.436 0(3)	0.378 2(5)
O(11)	0.481 0(4)	0.449 0(3)	0.311 9(5)	0.490 1(4)	0.447 0(3)	0.306 5(5)	0.487 4(4)	0.445 0(2)	0.311 1(5)
C(12)	0.346 0(5)	0.503 9(3)	0.523 5(6)	0.353 8(5)	0.506 9(4)	0.507 5(7)	0.354 0(4)	0.508 9(3)	0.511 0(5)
O(12)	0.339 8(4)	0.553 8(2)	0.534 6(5)	0.347 9(4)	0.557 5(3)	0.516 5(6)	0.348 4(4)	0.559 1(2)	0.517 4(5)
C(13)	0.438 6(4)	0.414 6(3)	0.620 5(6)	0.444 4(5)	0.416 9(4)	0.608 6(7)	0.443 3(4)	0.419 3(3)	0.612 5(5)
O(13)	0.482 5(3)	0.412 5(3)	0.692 0(5)	0.486 7(4)	0.415 0(3)	0.682 6(5)	0.486 5(3)	0.417 0(3)	0.685 7(5)
C(21)	0.414 8(4)	0.290 7(3)	0.589 6(6)	0.412 9(5)	0.295 6(4)	0.574 6(6)	0.410 8(4)	0.296 6(3)	0.581 4(5)
O(21)	0.435 4(3)	0.280 9(3)	0.679 1(4)	0.431 4(3)	0.285 0(3)	0.664 1(4)	0.429 0(3)	0.287 2(2)	0.671 0(3)
C(22)	0.492 2(5)	0.307 9(4)	0.399 4(7)	0.497 9(5)	0.308 5(4)	0.394 6(7)	0.495 8(4)	0.308 3(3)	0.398 6(5)
O(22)	0.556 6(4)	0.312 3(4)	0.384 8(6)	0.563 7(3)	0.309 4(4)	0.380 8(6)	0.561 9(3)	0.310 2(3)	0.387 5(5)
C(23)	0.377 0(4)	0.215 9(3)	0.419 7(7)	0.374 8(5)	0.221 0(4)	0.411 8(7)	0.374 1(4)	0.219 9(3)	0.418 7(6)
O(23)	0.371 7(4)	0.165 9(2)	0.415 6(6)	0.369 4(4)	0.170 5(3)	0.410 0(6)	0.367 4(4)	0.169 7(2)	0.419 0(5)
C(31)	0.219 8(5)	0.261 8(4)	0.476 3(6)	0.213 8(6)	0.268 4(4)	0.450 5(7)	0.212 3(5)	0.268 4(3)	0.452 3(6)
O(31)	0.199 2(4)	0.215 5(2)	0.456 4(5)	0.191 1(5)	0.222 2(3)	0.427 7(6)	0.191 7(4)	0.221 9(2)	0.431 6(5)
C(32)	0.145 4(5)	0.362 5(4)	0.558 8(8)	0.137 7(5)	0.367 1(4)	0.537 1(7)	0.136 0(4)	0.367 0(4)	0.539 7(6)
O(32)	0.081 0(4)	0.372 8(4)	0.576 3(8)	0.074 0(4)	0.376 4(4)	0.551 6(6)	0.071 4(3)	0.376 5(3)	0.550 9(6)
C(33)	0.265 6(5)	0.311 8(4)	0.677 4(6)	0.257 3(5)	0.307 2(4)	0.650 2(7)	0.254 7(4)	0.305 7(3)	0.654 4(5)
O(33)	0.272 5(4)	0.294 0(3)	0.766 7(4)	0.260 5(4)	0.284 4(3)	0.733 8(5)	0.257 3(4)	0.281 9(3)	0.737 2(4)
Phosphine ligands									
P(1)	0.260 06(11)	0.406 09(8)	0.382 06(15)	0.261 91(12)	0.412 10(9)	0.372 43(16)	0.261 43(9)	0.412 33(6)	0.375 89(11)
C(111)	0.189 7(4)	0.465 1(3)	0.355 0(5)	0.193 4(5)	0.473 2(3)	0.350 9(6)	0.192 2(4)	0.473 9(3)	0.352 7(4)
C(112)[a]	0.156 9(9)	0.486 9(7)	0.256 1(12)	0.177 8(6)	0.496 5(4)	0.251 1(7)	0.176 7(5)	0.496 9(3)	0.251 3(5)
C(113)[a]	0.104 0(9)	0.532 0(7)	0.240 9(13)	0.123 5(7)	0.543 6(5)	0.236 2(7)	0.125 1(6)	0.544 2(4)	0.235 2(6)
C(114)[a]	0.072 2(11)	0.557 3(7)	0.335 4(15)	0.087 4(6)	0.566 8(4)	0.321 3(7)	0.087 9 (5)	0.567 6(3)	0.320 2(6)
C(115)[a]	0.097 0(9)	0.539 8(7)	0.435 4(12)	0.103 7(6)	0.545 6(4)	0.422 1(7)	0.102 7(5)	0.546 5(3)	0.422 9(6)
C(116)[a]	0.151 2(9)	0.497 0(7)	0.447 1(11)	0.156 4(6)	0.499 5(4)	0.437 8(7)	0.156 3(5)	0.500 8(3)	0.437 1(5)
C(120)	0.282 7(4)	0.383 6(3)	0.238 1(6)	0.284 9(5)	0.390 7(3)	0.231 6(6)	0.285 5(3)	0.390 6(3)	0.235 6(4)
P(2)	0.334 18(12)	0.313 79(9)	0.250 84(15)	0.335 42(12)	0.319 88(9)	0.242 61(17)	0.334 96(9)	0.319 06(7)	0.248 22(11)
C(211)	0.393 6(4)	0.313 6(3)	0.132 8(5)	0.398 7(5)	0.320 2(4)	0.124 2(6)	0.398 3(4)	0.318 1(3)	0.129 7(4)
C(212)[b]	0.380 7(9)	0.352 3(7)	0.035 2(12)	0.369 8(11)	0.312 3(8)	0.023 1(15)	0.372 5(19)	0.315 1(14)	0.022 9(23)
C(213)[b]	0.427 2(10)	0.346 4(8)	−0.050 8(13)	0.411 0(11)	0.315 6(9)	−0.069 7(14)	0.410 4(28)	0.318 8(20)	−0.067 2(30)
C(214)[b]	0.494 6(5)	0.311 2(5)	−0.048 9(7)	0.498 0(12)	0.324 6(9)	−0.056 0(14)	0.494 6(26)	0.318 6(26)	−0.051 2(30)
C(215)[b]	0.525 0(13)	0.317 4(14)	0.047 0(19)	0.527 1(13)	0.338 6(10)	0.040 4(15)	0.523 3(10)	0.332 0(9)	0.045 0(14)
C(216)[b]	0.479 3(11)	0.313 0(13)	0.142 7(14)	0.477 9(9)	0.335 8(7)	0.131 6(11)	0.478 0(9)	0.331 0(8)	0.136 0(11)
C(212′)[b]	0.378 8(9)	0.311 9(9)	0.031 3(11)	0.369 2(10)	0.337 1(10)	0.024 3(12)	0.366 2(23)	0.339 7(16)	0.033 9(26)
C(213′)[b]	0.428 9(12)	0.312 4(9)	−0.061 8(12)	0.420 8(12)	0.334 9(10)	−0.065 8(13)	0.421 0(31)	0.334 8(26)	−0.057 9(33)
C(214′)[b]				0.486 7(11)	0.312 7(13)	−0.062 6(14)	0.483 6(23)	0.315 8(20)	−0.058 7(17)
C(215′)[b]	0.509 0(9)	0.272 0(7)	0.049 4(12)	0.512 6(12)	0.290 6(14)	0.038 2(16)	0.513 0(12)	0.280 5(11)	0.045 8(16)
C(216′)[b]	0.457 2(9)	0.275 7(7)	0.140 3(13)	0.471 9(12)	0.289 2(11)	0.130 7(16)	0.464 9(11)	0.286 1(9)	0.134 3(14)
C(221)	0.262 2(4)	0.259 9(3)	0.204 0(6)	0.261 1(5)	0.265 5(4)	0.198 0(6)	0.258 9(4)	0.266 7(3)	0.202 7(5)
C(222)	0.284 4(6)	0.208 2(5)	0.158 2(10)	0.283 3(5)	0.210 5(4)	0.169 4(8)	0.283 7(4)	0.209 7(3)	0.174 7(6)
C(223)	0.232 3(7)	0.165 1(6)	0.127 5(12)	0.229 7(6)	0.168 1(4)	0.139 0(9)	0.227 7(6)	0.166 9(4)	0.145 4(7)
C(224)	0.157 1(7)	0.174 7(5)	0.137 7(9)	0.151 5(6)	0.180 2(5)	0.137 4(9)	0.149 8(5)	0.180 7(4)	0.143 4(8)
C(225)	0.130 9(5)	0.225 9(5)	0.182 7(8)	0.128 3(6)	0.235 0(5)	0.169 6(10)	0.125.8(5)	0.235 3(4)	0.171 3(8)

Table 5 (*continued*)

Atom	(10) M = Cu x	y	z	(11) M = Ag x	y	z	(12) M = Au x	y	z
C(226)	0.185 8(5)	0.269 0(4)	0.215 9(7)	0.180 1(5)	0.279 1(4)	0.196 9(8)	0.181 6(4)	0.278 7(4)	0.202 0(7)
P(3)	0.223 40(12)	0.483 77(0)	0.797 88(17)	0.217 37(15)	0.487 17(11)	0.808 47(18)	0.217 44(10)	0.485 12(7)	0.805 26(12)
C(311)	0.292 1(4)	0.509 0(3)	0.903 3(6)	0.283 3(5)	0.514 8(4)	0.913 8(7)	0.285 3(4)	0.512 2(3)	0.909 4(5)
C(312)[a]	0.285 6(10)	0.557 4(7)	0.974 9(14)	0.268 4(6)	0.557 1(5)	0.985 3(8)	0.269 4(6)	0.555 0(4)	0.981 7(8)
C(313)[a]	0.342 1(13)	0.570 9(8)	1.051 9(14)	0.316 4(7)	0.571 5(5)	1.073 1(8)	0.319 8(6)	0.569 4(4)	1.067 8(7)
C(314)[a]	0.406 7(9)	0.539 0(10)	1.053 4(13)	0.381 6(8)	0.543 6(6)	1.089 7(12)	0.384 9(8)	0.541 1(6)	1.084 2(10)
C(315)[a]	0.404 4(10)	0.480 1(8)	1.017 9(16)	0.397 7(7)	0.495 3(6)	1 031 5(11)	0.398 7(7)	0.498 8(6)	1.027 0(10)
C(316)[a]	0.353 9(9)	0.469 1(7)	0.935 4(13)	0.348 9(7)	0.482 5(6)	0.934 4(9)	0.349 5(6)	0.480 0(6)	0.929 8(9)
C(321)	0.154 4(4)	0.442 5(3)	0.879 8(6)	0.148 3(5)	0.442 4(4)	0.885 3(6)	0.149 8(4)	0.441 0(3)	0.883 6(5)
C(322)[a]	0.085 6(9)	0.466 4(8)	0.906 2(14)	0.104 9(8)	0.461 1(5)	0.967 6(9)	0.107 6(7)	0.461 1(5)	0.967 0(8)
C(323)[a]	0.037 7(10)	0.432 7(10)	0.969 5(15)	0.061 1(7)	0.425 4(6)	1.027 9(9)	0.059 8(7)	0.423 3(5)	1.025 5(8)
C(324)	0.053 8(5)	0.374 5(5)	1.002 6(7)	0.050 9(7)	0.370 9(6)	1.000 7(9)	0.051 7(6)	0.370 3(5)	1.004 3(8)
C(325)[a]	0.125 5(10)	0.351 1(8)	0.964 3(14)	0.091 4(13)	0.350 6(7)	0.921 8(16)	0.091 0(15)	0.350 5(7)	0.920 1(16)
C(326)[a]	0.174 6(9)	0.386 8(7)	0.905 6(12)	0.140 0(10)	0.386 5(6)	0.861 5(12)	0.139 9(12)	0.385 1(6)	0.862 3(14)
C(331)[a]	0.171 7(5)	0.549 7(3)	0.752 2(7)	0.161 4(6)	0.551 4(4)	0.761 5(7)	0.160 1(5)	0.548 9(3)	0.759 2(5)
C(332)[a]	0.088 9(9)	0.553 4(8)	0.760 6(12)	0.082 2(6)	0.548 4(5)	0.741 5(9)	0.082 5(6)	0.545 7(5)	0.738 9(7)
C(333)[a]	0.048 5(13)	0.600 9(9)	0.722 7(16)	0.039 1(7)	0.597 2(7)	0.697 2(9)	0.041 2(7)	0.595 9(6)	0.700 2(9)
C(334)[a]	0.082 1(11)	0.639 8(7)	0.665 7(18)	0.081 5(10)	0.644 9(6)	0.678 6(11)	0.077 3(10)	0.644 3(5)	0.675 8(8)
C(335)[a]	0.170 2(16)	0.649 6(8)	0.6801 (17)	0.158 6(11)	0.651 8(5)	0.691 6(13)	0.153 0(13)	0.648 7(5)	0.693 4(14)
C(336)[a]	0.209 7(13)	0.597 7(7)	0.723 8(14)	0.198 6(9)	0.602 2(5)	0.735 9(12)	0.200 3(9)	0.600 6(5)	0.731 0(11)

Additional disordered components [(**10**) only]; populations of all components are 0.5

	x	y	z		x	y	z
C(112′)	0.221 8(9)	0.512 0(7)	0.303 9(13)	C(322′)	0.140 6(9)	0.452 4(8)	0.999 5(12)
C(113′)	0.169 9(11)	0.556 5(7)	0.269 8(13)	C(323′)	0.087 1(10)	0.417 5(8)	1.056 6(13)
C(114′)	0.091 6(9)	0.553 2(7)	0.288 1(14)	C(325′)	0.063 9(11)	0.362 9(8)	0.895 8(15)
C(115′)	0.068 3(10)	0.501 5(9)	0.333 0(17)	C(326′)	0.116 1(10)	0.395 4(7)	0.840 1(15)
C(116′)	0.119 2(9)	0.455 3(7)	0.363 5(12)	C(332′)	0.144 8(10)	0.550 8(8)	0.635 0(13)
C(312′)	0.274 4(10)	0.521 2(9)	1.004 5(12)	C(333′)	0.107 0(12)	0.600 2(9)	0.590 4(14)
C(313′)	0.325 2(10)	0.545 4(9)	1.082 5(12)	C(334′)	0.105 3(15)	0.654 5(8)	0.676 8(14)
C(314′)	0.382 3(10)	0.540 7(9)	1.089 8(13)	C(335′)	0.130 8(14)	0.649 4(8)	0.751 7(18)
C(315′)	0.419 4(12)	0.547 0(11)	0.946 3(18)	C(336′)	0.172 4(13)	0.598 0(9)	0.797 4(16)
C(316′)	0.365 1(10)	0.522 8(10)	0.866 5(13)				

[a] Population: 0.5 [(**10**) only]. [b] Population: 0.5.

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