

Structural, spectroscopic and redox studies of *mer*-[RuX₃L₃] (L = PMe₂Ph or AsMe₂Ph, X = Cl or Br). Crystal structures of *mer*-[RuX₃(AsMe₂Ph)₃] (X = Cl or Br) and [Ru₂X₅(EMe₂Ph)₄] (X = Br, E = P or As; X = I, E = As)

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The complexes *mer*-[RuX₃L₃] (X = Cl or Br, L = PMe₂Ph or AsMe₂Ph) have been re-examined and assignments for their UV/VIS spectra proposed. Attempts to prepare analogues with X = I or L = SbR₃ have been unsuccessful. Cyclic voltammetry revealed only irreversible oxidation and reduction processes and chemical oxidation with halogens resulted in decomposition to [RuX₆]²⁻, in contrast to the chemistry of related osmium compounds. The crystal structures of *mer*-[RuX₃(AsMe₂Ph)₃] (X = Cl or Br) have been determined and confirm the geometrical isomer formed. Crystal structures were also determined for [Ru₂X₅L₄] (X = Br, L = PMe₂Ph or AsMe₂Ph; X = I, L = AsMe₂Ph) obtained by decomposition of *mer*-[RuX₃L₃] in solution, which are the first structurally characterised examples of Ru₂⁵⁺ dimers of this type with bromide or iodide co-ligands. The structures are consistent with a formal Ru–Ru bond order of $\frac{1}{2}$.

In previous studies we have described the effects of systematic variation of both neutral and halide ligands upon the stability, spectroscopic properties and redox chemistry of several series of osmium complexes including *trans*-[OsX₄L₂]^{0/-} (ref. 1), *mer*-[OsX₃L₃]^{0/+} (ref. 2) and *trans*-[OsX₂L₄]^{0/+2+} (ref. 3) (L = PR₃, AsR₃ or SbR₃; X = Cl or Br, sometimes I). Limited information is available for ruthenium complexes with monodentate ligands, in part because of the much greater reactivity and their tendency to rearrange into halide-bridged dimers.^{4,5} Here we report studies of representative *mer*-[RuX₃L₃] complexes and the structures of some mixed-valence Ru^{II}–Ru^{III} dimers formed by their decomposition.

Results and Discussion

Synthesis and properties

The complexes *mer*-[RuCl₃L₃] (L = PMe₂Ph or AsMe₂Ph) were made by reaction of RuCl₃·xH₂O with the ligand in ethanol-concentrated HCl and converted into the bromides by metathesis with LiBr.⁶ Only one example of a *mer*-[RuI₃L₃] (L = AsMe₂Ph) is mentioned in the literature,⁷ made by reaction of AsMe₂Ph₂ with K₂[RuCl₅(H₂O)] and KI in ethanol and with little characterisation. In our hands repeated attempts to make *mer*-[RuI₃L₃] (L = PMe₂Ph or AsMe₂Ph) by metathesis of the chloro complexes with LiI in a variety of solvents failed, the major products being ruthenium(II) complexes of type *trans*-[Ru₂L₄], along with smaller amounts of other uncharacterised ruthenium species. *In situ* monitoring of the UV/VIS spectra of these reactions showed the rapid development of species with intense absorptions at ca. 10 000 cm⁻¹, which are probably I(π)→Ru^{III}(t_{2g}) charge-transfer (CT) bands,⁸ but the spectra rapidly decay into ones characteristic of Ru^{II}. The reaction of [Ru(dmff)₆]³⁺ (dmf = dimethylformamide)⁹ with L and LiI in ethanol also gave *trans*-[RuI₂L₄]¹⁰ along with some [Ru₂I₃L₄] (see below). It seems possible that *mer*-[RuI₃L₃] may form transiently, but decompose too rapidly to be isolated. In a similar vein, reaction of RuX₃·xH₂O (X = Cl or Br) with SbMe₂Ph under a variety of conditions gave *trans*-[RuX₂(SbMe₂Ph)₄]¹⁰ as major products and no examples of *mer*-[RuX₃(SbR₃)₃] are known.†

† We have shown elsewhere¹¹ that whilst *trans*-[RuCl₂(SbPh₃)₄]BF₄ can be made, there is no good evidence for *mer*-[RuCl₃(SbPh₃)₃], although osmium(III) analogues are well characterised.²

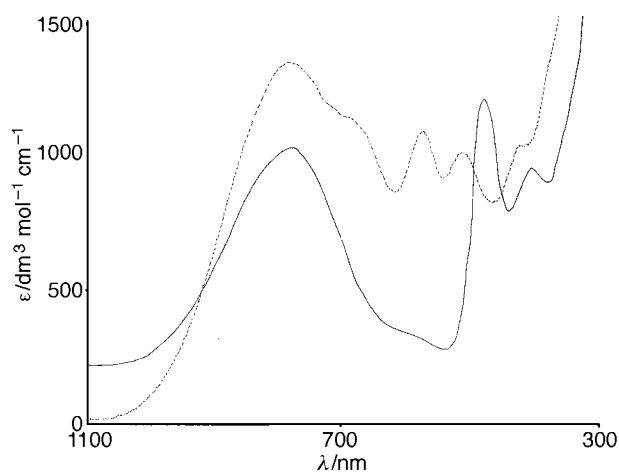


Fig. 1 The UV/VIS spectra of *mer*-[RuX₃(AsMe₂Ph)₃] [X = Cl (—) or Br (---)] in CH₂Cl₂

The IR and ESR spectra of the *mer*-[RuX₃L₃] complexes (Experimental section) are in agreement with literature data.¹² Electrospray mass spectrometry (MeCN solution) gave features with the appropriate isotope patterns for [RuX₂L₃]⁺, [RuX₂L₂]⁺ and [RuXL₃]⁺ ions. The rich UV/VIS spectra of these complexes are listed in Table 1 and examples are shown in Fig. 1. The assignments of the major features in terms of ligand-to-metal CT transitions in C_{2v} symmetry follows from those of the analogous *mer*-[OsX₃L₃].² For the osmium complexes corresponding bands are found ca. 3000–4000 cm⁻¹ to high energy compared with the ruthenium complexes, reflecting the greater ease of reduction of the latter. For osmium a small number of *fac*-[OsCl₃L₃] (L = PMe₂Ph, PEt₂Ph or AsMe₂Ph) are known,^{2,6,13} but no ruthenium analogues have been characterised. Our attempts to convert *mer*-[RuCl₃L₃] into the *fac* isomer, by sequential treatment with NaBH₄ and HCl (as used for the osmium complexes),¹³ failed and *mer*-[RuCl₃L₃] in toluene were not isomerised by photolysis (254 nm, 96 h).

Crystal structures of *mer*-[RuX₃(AsMe₂Ph)₃] (X = Cl or Br)

The two compounds are isomorphous and are shown by the X-ray study to be the *mer* geometrical isomer with angles at the Ru atom within 9° of the idealised octahedral values (see Fig. 2 and Table 2). Despite the fact that *mer*-[RuX₃L₃] compounds

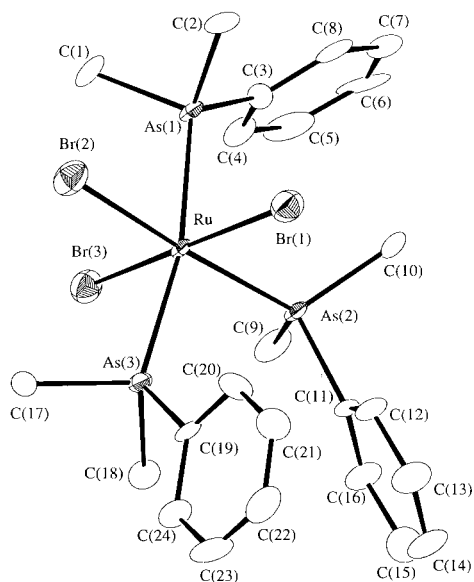
Table 1 The UV/VIS data for the *mer*-[RuX₃L₃] complexes^a

Complex	$\sigma(\text{L}) \longrightarrow t_{2g}(\text{Ru})$	$\sigma(\text{L}) + \sigma(\text{X}) \longrightarrow t_{2g}(\text{Ru})$	$\pi(\text{X}) \longrightarrow t_{2g}(\text{Ru})$	Others ^b
[RuCl ₃ (PMe ₂ Ph) ₃]	15.6 (240)	19.7 (1 460)	22.9 (990)	35.8 (21 160), 38.8 (16 250)
[RuBr ₃ (PMe ₂ Ph) ₃]	14.5 (780)	16.5 (sh) (900)	18.1 (1000), 22.5 (840)	34.5 (12 500), 38.2 (15 000)
[RuCl ₃ (AsMe ₂ Ph) ₃]	12.6 (1290), 15.3 (sh)	20.0 (1500)	23.2 (1140)	34.0 (14 770), 38.2 (19 900)
[RuBr ₃ (AsMe ₂ Ph) ₃]	12.5 (1360), 14.1 (sh)	16.8 (1230)	18.8 (1160), 22.3 (970)	32.6 (13 300), 36.5 (17 450)

^a $E_{\text{max}}/10^3 \text{ cm}^{-1}$ ($\epsilon_{\text{mol}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in CH₂Cl₂ solution. ^b $\pi \rightarrow \pi^*$ of aryl rings will occur in this region.

Table 2 Selected bond lengths (Å) and angles (°) for *mer*-[RuX₃(AsMe₂Ph)₃] (X = Cl or Br)

	X = Cl	X = Br
Ru–X(1)	2.339(5)	2.461(2)
Ru–X(2)	2.387(5)	2.513(2)
Ru–X(3)	2.345(5)	2.476(2)
Ru–As(1)	2.456(2)	2.467(2)
Ru–As(2)	2.473(2)	2.482(2)
Ru–As(3)	2.495(2)	2.509(2)
As–C	1.90(2)–1.97(2)	1.91(1)–1.96(1)
C–C	1.36(3)–1.40(2)	1.35(2)–1.42(2)
X(1)–Ru–X(2)	92.2(2)	91.7(1)
X(1)–Ru–X(3)	173.2(2)	173.0(1)
X(2)–Ru–X(3)	93.8(2)	93.7(1)
As(1)–Ru–As(2)	95.9(1)	96.8(1)
As(1)–Ru–As(3)	168.4(1)	168.6(1)
As(2)–Ru–As(3)	93.0(1)	92.2(1)
X(1)–Ru–As(1)	89.3(1)	88.4(1)
X(1)–Ru–As(2)	84.6(1)	85.1(1)
X(1)–Ru–As(3)	98.9(1)	99.4(1)
X(2)–Ru–As(1)	82.5(1)	81.8(1)
X(2)–Ru–As(2)	176.5(1)	176.5(1)
X(2)–Ru–As(3)	88.9(1)	89.6(1)
X(3)–Ru–As(1)	88.1(1)	88.0(1)
X(3)–Ru–As(2)	89.3(1)	89.4(1)
X(3)–Ru–As(3)	84.6(1)	85.0(1)

**Fig. 2** The structure of *mer*-[RuBr₃(AsMe₂Ph)₃] showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The corresponding chloro compound has essentially the same structure

have long been known and are useful precursors to other ruthenium complexes, none has been structurally characterised, although with nitrogen donors there are a few examples of octahedral ruthenium(III) chloro complexes. There are also a few examples^{14–16} of the anionic ruthenium(III) species *trans*-[RuCl₄(PR₃)₂][−] (R = Et, Bu or Ph). The Ru–Cl distances in the present compound [2.339(5)–2.387(5) Å] appear typical and may be compared¹⁴ with 2.367(4) and 2.361(4) Å found in

trans-[RuCl₄(PEt₃)₂][−]. Structurally determined Ru–As bonds are rare and the present values [2.456(2)–2.509(2) Å] can be compared¹⁷ with those in *trans*-[RuBr₂{C₆F₄(AsMe₂)₂-o₂}⁺] [2.457(1), 2.460(1) Å] and this cation provides a comparator Ru–Br distance [2.455(1) Å].

Redox chemistry

An initial aim of this study was to probe the redox chemistry of *mer*-[RuX₃L₃] type complexes. As background it is useful to recall that the osmium(III) analogues *mer*-[OsX₃L₃] undergo irreversible one-electron reductions to osmium(II) species which readily undergo halide substitution and/or dimerisation depending upon the conditions.¹⁸ In contrast electrochemically reversible one-electron oxidation produces *mer*-[OsX₃L₃]⁺, which can be isolated as BF₄[−] salts by HNO₃–HBF₄ treatment of *mer*-[OsX₃L₃].² Cyclic voltammetric studies of *mer*-[RuX₃L₃] in CH₂Cl₂ containing 0.2 mol dm^{−3} [NBu₄][BF₄] at scan rates of 0.02–0.2 V s^{−1} showed completely irreversible reduction and oxidation processes at *ca.* +0.1 and +1.4 V (*versus* ferrocene/ferrocenium at +0.58 V) showing that neither [RuX₃L₃]^{+/−} are stable on this time-scale. Attempted chemical oxidation was also unsuccessful. Addition of the appropriate halogen in CCl₄ to CH₂Cl₂ solutions of *mer*-[RuX₃L₃] produced immediate colour changes, but the UV/VIS spectra identified the ruthenium product as the corresponding [RuX₆]^{2−},¹⁹ whilst the solid complexes decolourised rapidly when added to concentrated HNO₃–HBF₄ at 0 °C.

Crystal structures of [Ru₂X₅(EMe₂Ph)₄] (X = Br, E = P or As; X = I, E = As)

During the attempted crystallisation of several of the *mer* species described above, there were often crystals formed with the same colour but two distinct morphologies. Typically a few large block crystals formed in the presence of many smaller rhombic shaped ones. Hand selection and X-ray examination of these smaller crystals established that the structures were dinuclear. In the iodo case below the dinuclear product was obtained from the solution decomposition of *trans*-[Ru₂(AsMe₂Ph)₄] during crystal growth. We now report the structure of the following three species: [Ru₂Br₅(PMe₂Ph)₄], [Ru₂Br₅(AsMe₂Ph)₄] and [Ru₂I₅(AsMe₂Ph)₄]. The chloro species [Ru₂Cl₅(PMe₂Ph)₄] also formed in this way and was identified by comparison with the unit-cell dimensions previously reported.¹⁵ All three compounds are of the Ru^{II}–Ru^{III} mixed-valence type and are isomorphous. The [Ru₂Br₅(PMe₂Ph)₄] compound is shown in Fig. 3 and selected bond lengths and angles in Table 3. It was refined in the space group *C2/c* where the molecule has *C*₂ crystallographic symmetry and is isomorphous with the chloro compound.¹⁵ The Ru–Ru distance [3.083(2) Å] is longer and the Ru–Br–Ru angles are more acute [73.24(6), 74.01(5)°] than the chloro derivative [2.9941(4) Å, 74.41(4) and 75.41(3)° respectively]. As expected the terminal Ru–Br is shorter than the bridging distances and the bridging bromine not on the two-fold axis is bonded unsymmetrically to the Ru atoms (0.12 Å difference).

The compounds [Ru₂Br₅(AsMe₂Ph)₄] and [Ru₂I₅(AsMe₂Ph)₄] were again refined in the space group *C2/c* and key structural parameters are shown in Table 3 (see also Fig. 3). As commented on recently²⁰ for Ru^{II}–Ru^{II} species [Ru₂X₃L₆]⁺, the

Table 3 Selected bond lengths (Å) and angles (°) for [Ru₂X₅(EMe₂Ph)₄] (X = Br or I, E = P or As)*

	X = Br, E = P	X = Br, E = As	X = I, E = As
Ru–Ru'	3.083(2)	2.941(2)	3.197(5)
Ru–X(br 1)	2.585(2)	2.528(2)	2.712(4)
Ru–X(br 2)	2.501(1)	2.473(2)	2.677(3)
Ru'–X(br 2)	2.619(2)	2.546(2)	2.738(4)
Ru–X(t)	2.486(2)	2.431(2)	2.714(3)
Ru–E(1)	2.311(3)	2.405(1)	2.435(4)
Ru–E(2)	2.310(3)	2.410(2)	2.430(5)
E–C	1.81(1)–1.83(1)	1.92(1)–1.96(1)	1.95(3)–2.00(3)
Ru–X(br 1)–Ru'	73.2(1)	71.1(1)	72.2(1)
Ru–X(br 2)–Ru'	74.0(1)	71.7(1)	72.3(1)
X(br 2)–Ru–X(t)	178.0(1)	178.1(1)	176.9(1)

* t = terminal, br = bridge (br 1 on two-fold axis). Symmetry labels: (') 1 - x, y, ½ - z [1 - x, y, ½ - z (X/E = Br/As only)].

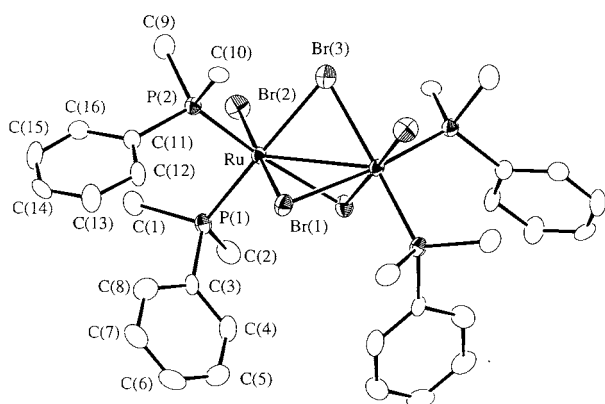


Fig. 3 The structure of [Ru₂Br₅(PMe₂Ph)₄] showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The two other compounds [Ru₂Br₅(AsMe₂Ph)₄] and [Ru₂I₅(AsMe₂Ph)₄] have essentially the same structure

replacement of P by As results in a shorter Ru–Ru and the same trend is observed for these mixed-valence compounds. The Ru–X–Ru angles for X = I are about the same (72°) as for X = Br and this together with the longer Ru–I bonds results in an increased Ru–Ru distance [3.197(5) Å].

The [Ru₂Cl₅(PMe₂Ph)₄] complex has been studied in some detail by Cotton and Torralba,¹⁵ and the compounds reported here are the first examples of bromide and iodide analogues. Although obtained serendipitously and at present in too small yield for detailed spectroscopic study, the structures strongly suggest that they can be regarded as having a metal oxidation state of 2.5, with a delocalised electron and a formal Ru–Ru bond order of ½. As would be expected, the Ru–Ru distance varies with the identity of the bridging halide from 2.99 (X = Cl)¹⁵ to 3.20 Å (I), but even in the latter the distance is shorter than in the unsymmetrical dimer [(Bu₃P)₃RuCl₃–RuCl₂(PBu₃)] (3.28 Å)¹⁵ which is considered as valence-trapped Ru^{II}–Ru^{III} with no metal–metal bond.

Experimental

Physical measurements were made as described previously.² Electrospray mass spectra were obtained using a Hewlett-Packard series 1050 mass spectrometer operating in positive electrospray mode using solutions in MeCN and ESR spectra from powdered solids at 150 K on a Bruker ECS 106 spectrometer.

Preparations

mer-[RuCl₃(PMe₂Ph)₃]. The compound RuCl₃·xH₂O (0.63 g, 2.4 mmol) was dissolved in ethanol (30 cm³) along with concen-

trated HCl (1 cm³). To this PMe₂Ph (0.98 g, 7.1 mmol) was added and the mixture heated to reflux under nitrogen for ca. 5 min and then cooled. A brown solid separated from the solution and was filtered off, washed with diethyl ether (2 × 15 cm³) and dried *in vacuo* (0.72 g, 48% based on RuCl₃·xH₂O) (Found: C, 46.1; H, 5.2. Calc. for C₂₄H₃₃Cl₃P₃Ru: C, 46.3; H, 5.4%). ν(Ru–Cl)/cm⁻¹ (Nujol mull) 327, 300 and 270. Electrospray mass spectrum: *m/z* = 586, 550 (calc. for C₂₄H₃₃³⁵Cl₂P₃¹⁰¹Ru 585, C₂₄H₃₃³⁵ClP₃¹⁰¹Ru 550).

mer-[RuBr₃(PMe₂Ph)₃]. The complex mer-[RuCl₃(PMe₂Ph)₃] (0.53 g, 0.85 mmol) was suspended in ethanol (30 cm³). To this LiBr (1.77 g, 20 mmol) was added and the mixture heated to reflux under nitrogen for ca. 10 min and then cooled. A deep purple solid separated from a similar coloured solution and was filtered off, washed with water (2 × 10 cm³) and dried *in vacuo* (0.38 g, 59%) (Found: C, 37.9; H, 4.1. Calc. for C₂₄H₃₃Br₃P₃Ru: C, 38.2; H, 4.4%). ν(Ru–Br)/cm⁻¹ (Nujol mull) 242 and 225. Electrospray mass spectrum: *m/z* = 675, 595 and 537 (calc. for C₂₄H₃₃⁷⁹Br₂P₃¹⁰¹Ru 673, C₂₄H₃₃⁷⁹BrP₃¹⁰¹Ru 594, C₁₆H₂₂⁷⁹Br₂P₂¹⁰¹Ru 535).

mer-[RuCl₃(AsMe₂Ph)₃]. The compound RuCl₃·xH₂O (1.28 g, 4.90 mmol) was dissolved in ethanol (25 cm³) along with concentrated HCl (2.5 cm³). To this AsMe₂Ph (3.33 g, 18.3 mmol) was added and the mixture heated to reflux under nitrogen for ca. 1 h and then cooled. A dark green solid separated which was filtered off, washed with diethyl ether (2 × 15 cm³) and dried *in vacuo* (3.07 g, 83%) (Found: C, 38.3; H, 4.1. Calc. for C₂₄H₃₃As₃Cl₃Ru: C, 38.3; H, 3.8%). ν(Ru–Cl)/cm⁻¹ (Nujol mull) 323, 310 and 270. ESR (powdered solid 150 K): *g* = 2.27, 2.05 and 1.92. Electrospray mass spectrum: *m/z* = 718, 682 and 536 (calc. for C₂₄H₃₃As₃³⁵Cl₂¹⁰¹Ru 717, C₂₄H₃₃As₃³⁵Cl¹⁰¹Ru 682, C₁₆H₂₂As₂³⁵Cl₂¹⁰¹Ru 535).

mer-[RuBr₃(AsMe₂Ph)₃]. The complex mer-[RuCl₃–(AsMe₂Ph)₃] (1.0 g, 1.33 mmol) was suspended in ethanol (30 cm³). To this LiBr (2.30 g, 26.4 mmol) was added and the mixture heated to reflux under nitrogen for ca. 10 min and then cooled. A black solid separated and was filtered off, washed with water (2 × 10 cm³) and dried *in vacuo* (0.8 g, 68%) (Found: C, 33.0; H, 3.6. Calc. for C₂₄H₃₃As₃Br₃Ru: C, 32.5; H, 3.8%). ν(Ru–Br)/cm⁻¹ 252, 226 and 197. ESR (powdered solid 150 K): *g* = 2.27, 2.06 and 1.91. Electrospray mass spectrum: *m/z* = 807, 727 and 625 (calc. for C₂₄H₃₃As₃⁷⁹Br₂¹⁰¹Ru 805, C₂₄H₃₃As₃⁷⁹Br¹⁰¹Ru 726, C₁₆H₂₂As₂⁷⁹Br₂¹⁰¹Ru 625).

Crystallography

Details of the crystallographic studies are presented in Table 4. Data were collected on a Rigaku AFC7S diffractometer equipped with Mo-Kα radiation (λ = 0.710 69 Å) and a graphite monochromator. Selected crystals were mounted on glass fibres following oil immersion and held at 150 K using an Oxford Cryosystems low-temperature device. The Lorentz-polarisation corrections and any correction for the small amount of decay were applied during data reduction. Crystal solution was by means of SHELXS 86²¹ and full-matrix least-squares refinement on *F* was carried out with the TEXSAN package.²² The space group of the binuclear systems was either *Cc* or *C2/c* with the *N*(*z*) test favouring the centrosymmetric space group and the analysis was successfully carried out in this space group. Some of the thermal ellipsoids of the carbon atoms were suggestive of disorder although individual atom sites could not be recognised. This problem could be associated with the empirical absorption corrections used and the rather large μ values, genuine disorder, or the possibility of the lower-symmetry space group as difficulties over the choice of *Cc* versus *C2/c* are well known.²³ Hydrogen atoms were usually included in the model at calculated positions [*d*(C–H) = 0.95 Å]. Other details for individual structures are as follows.

Table 4 Crystallographic details*

	<i>mer</i> -[RuCl ₃ (AsMe ₂ -Ph) ₃]	<i>mer</i> -[RuBr ₃ (AsMe ₂ -Ph) ₃]	[Ru ₂ Br ₅ (PMe ₂ -Ph) ₄]	[Ru ₂ Br ₅ (AsMe ₂ -Ph) ₄]	[Ru ₂ I ₅ (AsMe ₂ Ph) ₄]
Formula	C ₂₄ H ₃₃ As ₃ Cl ₃ Ru	C ₂₄ H ₃₃ As ₃ Br ₃ Ru	C ₃₅ H ₄₄ Br ₅ P ₄ Ru ₂	C ₃₅ H ₄₄ As ₄ Br ₅ Ru ₂	C ₃₂ H ₄₄ As ₄ I ₅ Ru ₂
<i>M_r</i>	753.72	887.07	1154.25	1330.05	1565.05
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>C</i> 2/ <i>c</i> (no. 15)	<i>C</i> 2/ <i>c</i> (no. 15)	<i>C</i> 2/ <i>c</i> (no. 15)
<i>a</i> /Å	16.070(3)	16.112(7)	16.268(9)	15.978(6)	16.214(5)
<i>b</i> /Å	10.358(4)	10.380(2)	11.200(41)	11.508(4)	12.228(4)
<i>c</i> /Å	18.120(4)	18.206(6)	21.479(7)	21.421(7)	22.592(8)
β/°	113.68(2)	112.32(3)	102.66(3)	101.28(3)	113.32(2)
<i>U</i> /Å ³	2762(1)	2816(2)	3818(13)	3862(2)	4113(2)
2θ Range for cell/°	19.0–21.0	19.0–21.0	26.6–38.2	18.8–22.2	19.0–22.8
<i>D_c</i> /g cm ⁻³	1.812	2.091	2.008	2.287	2.526
<i>F</i> (000)	1484	1700	2236	2524	2884
Crystal size/mm	0.30 × 0.20 × 0.10	0.80 × 0.60 × 0.40	0.3 × 0.4 × 0.2	0.10 × 0.25 × 0.20	0.40 × 0.30 × 0.03
Total no. observations	5368	5465	3702	3731	3957
No. unique observations (<i>R_{int}</i>)	5175 (0.079)	5268 (0.060)	3566 (0.045)	3592 (0.031)	3810 (0.21)
Absorption correction	ψ Scan	ψ Scan	ψ Scan	DIFABS ²⁴	DIFABS
Maximum, minimum transmission	0.79, 1.00	0.463, 1.000	0.734, 1.000	0.615, 1.000	0.634, 1.000
No. data in refinement	2645 [<i>I</i> > 4σ(<i>I</i>)]	3577 [<i>I</i> > 3σ(<i>I</i>)]	2083 [<i>I</i> > 3σ(<i>I</i>)]	2203 [<i>I</i> > 4σ(<i>I</i>)]	1750 [<i>I</i> > 3σ(<i>I</i>)]
No. parameters	240	270	195	195	115
μ/cm ⁻¹	44.37	82.3	62.30	93.95	77.25
<i>hkl</i> Ranges	0–19, 0–12, –21 to 19	0–19, 0–12, –21 to 20	0–19, 0–13, –25 to 24	0–18, 0–13, –25 to 24	0–19, 0–14, –26 to 24
<i>S</i>	2.66	3.37	1.75	1.94	2.49
Maximum shift/e.s.d.	0.05	0.07	0.03	0.01	0.00
Residual electron density/e Å ⁻³	2.11 to –2.53	2.01 to –1.82	1.19 to –1.41	0.91 to –1.47	1.54 to –1.47
<i>R</i>	0.061	0.052	0.043	0.044	0.052
<i>R'</i>	0.081	0.057	0.053	0.055	0.071

* In common: monoclinic; *T* = 150 K; *Z* = 4; scan mode ω–2θ; *w*⁻¹ = σ²(*F_o*); maximum 2θ = 50°; *R* = Σ||*F_o* – |*F_c*||/Σ|*F_o*|; *R'* = [Σ*w*(*F_o* – *F_c*)²/Σ*wF_o*²]^{1/2}.

***mer*-[RuCl₃(AsMe₂Ph)₃]**. Dark brown crystals were obtained by liquid diffusion of EtOH into a CH₂Cl₂ solution of the target material. Eight C atoms were treated as isotropic since anisotropic thermal parameters resulted in non-positive definite ellipsoids indicative of possible disorder problems.

***mer*-[RuBr₃(AsMe₂Ph)₃]**. Dark brown crystals were obtained as above. Two C atoms were treated as isotropic (see comments above).

[Ru₂Br₅(PMe₂Ph)₄]. Dark brown crystals were obtained by liquid diffusion of EtOH into a CH₂Cl₂ solution of *mer*-[RuBr₃(PMe₂Ph)₃]. All C atoms were treated as anisotropic.

[Ru₂Br₅(AsMe₂Ph)₄]. Dark brown crystals were obtained by liquid diffusion of EtOH into a CH₂Cl₂ solution of *mer*-[RuBr₃(AsMe₂Ph)₃]. All C atoms were treated as anisotropic.

[Ru₂I₅(AsMe₂Ph)₄]. Dark brown crystals were obtained by liquid diffusion of EtOH into a CH₂Cl₂ solution of [RuI₂(AsMe₂Ph)₄]. Crystal decay was observed (8.5%). The carbon atoms were retained with isotropic thermal parameters as anisotropic ones gave no improved fit to the data and a few non-positive definite ellipsoids. No H atoms were included in the model.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/529.

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