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Synthesis and characterization of high-nuclearity iridium–ruthenium and –gold mixed-metal carbonyl clusters, $[Ir_7Ru_3(CO)_{23}]^-$, $[Ir_7Ru_3(CO)_{23}(AuPPh_3)]$ and $[Ir_6Ru_3(CO)_{21}(AuPPh_3)]^-$, possessing tetrahedrally capped octahedral iridium cores obtained by capping reactions with $[Ru_3(CO)_{12}]$ and $[AuCl(PPh_3)]$

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The new carbonyl cluster $[PPh_4][Ir_7Ru_3(CO)_{23}]$ **1** has been obtained by the high yield reaction of $[PPh_4]_2[Ir_6(CO)_{15}]$ with $[Ru_3(CO)_{12}]$ in the presence of *p*-toluenesulfonic acid. The monoanionic decanuclear cluster **1** has an octahedral arrangement of the iridium atoms with three ruthenium atoms and an iridium atom tetrahedrally capping four triangular faces. Two terminal CO ligands are bound to each iridium atom and three to each ruthenium atom. In this synthesis *p*-toluenesulfonic acid served as a degradation reagent for $[Ir_6(CO)_{15}]^{2-}$ to generate the capping $\{Ir(CO)_2\}^+$ moiety. Reaction of **1** with $[AuCl(PPh_3)]$ in the presence of $AgOSO_2CF_3$ at ambient temperature yielded the undecanuclear neutral cluster $[Ir_7Ru_3(CO)_{23}(AuPPh_3)]$ **2**. The $\{AuPPh_3\}^+$ group co-ordinates to the apical iridium atom of the parent metal carbonyl monoanion **1** maintaining the cluster framework as well as the stereogeometry of the CO ligands. Thermal treatment of **1** with $[AuCl(PPh_3)]$ in refluxing 1,2-dichloroethane caused substitution of the capping $\{Ir(CO)_2\}^+$ group in **1** with an isolobal $\{AuPPh_3\}^+$ group, resulting in the formation of decanuclear monoanionic cluster $[PPh_4][Ir_6Ru_3(CO)_{21}(AuPPh_3)]$ **3**.

Introduction

The most symmetric decanuclear clusters have the shape of a tetrahedron formed by capping of the central octahedral unit with four metal atoms. Non-carbonyl cluster complexes $[Hg_6Rh_4(PMe_3)_{12}]$,[1] $[Hg_6Pt_4(dipb)_4]$ (dipb = $(i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2$)[2] and $[Cu_6Re_4H_{24}(PPh_3)_8]^{2+}$[3] have been reported. $[Cu_6Fe_4(CO)_{16}]^{2-}$[4] is an example of a carbonyl cluster which is important as a model of CO adsorption on the surface of cubic close-packed (ccp) metal arrays. Although various clusters have been reported, the systematic synthesis of high-nuclear mixed metal carbonyls has proved to be difficult. Most of the reported clusters are incidental products obtained in very small amounts, and their determination is restricted to single crystal structure analysis.

Several decanuclear osmium carbonyl clusters of large tetrahedral metal cores, *e.g.* $[Os_{10}H_2C(CO)_{24}]$[5] and $[Os_{10}C(CO)_{24}]^{2-}$,[6] have been synthesized by pyrolysis of $[Os_3(CO)_{12}]$ or $[Os_3(CO)_{11}(py)]$. Pyrolysis of $[Os_3(CO)_{10}(NCMe)_2]$ at temperatures above 260 °C under vacuum led to the larger cluster $[Os_{20}(CO)_{40}]$ of the same T_d symmetry.[7] This thermolytic method is also applicable to synthesis of the corresponding decanuclear ruthenium cluster $[Ru_{10}N(CO)_{24}]^-$, which had been obtained directly from $[Ru_3(CO)_{12}]$ by reaction with 1/3 equivalent of $[N(PPh_3)_2][N_3]$ under thermolysis in bis(2-methoxyethyl) ether (diglyme).[8,9] The improved synthesis of the decanuclear nitridoruthenium cluster is slightly different from that of osmium. We previously reported a high-yield reproducible synthesis of the decaruthenium carbido dianion $[Ru_{10}C(CO)_{24}]^{2-}$ by redox condensation of the interstitial carbido dianion $[Ru_6C(CO)_{16}]^{2-}$ with $[Ru_3(CO)_{12}]$.[10] In the same way, the decaruthenium nitrido cluster $[Ru_{10}N(CO)_{24}]^-$ has selectively been obtained from $[Ru_6N(CO)_{16}]^-$ and $[Ru_3(CO)_{12}]$. In both cases a neutral $\{Ru(CO)_3\}$ unit produced by pyrolysis of $[Ru_3(CO)_{12}]$, which is unstable above 120 °C in both solution and the solid state, capped the octahedron of the Ru_6 cluster framework. The compound $[Ru_3(CO)_{12}]$ has a rich chemistry in homogeneous catalysis due to the active Ru–Ru bonds.[11]

However, the reaction of the interstitial hexaruthenium species with $[Ru_3(CO)_{12}]$ did not prove to be a generally applicable route to tetracapped octahedral clusters.[9] Various metals form clusters with an octahedral metal framework.[12] The dianionic iridium complex $[Ir_6(CO)_{15}]^{2-}$[13] is one example. This complex was chosen as a starting material for the synthesis of mixed metal clusters by thermolytic reaction with $[Ru_3(CO)_{12}]$ because of its thermal stability up to 200 °C, easy accessibility and possession of negative charges for redox condensation. Many examples of Ir–Ru mixed metal clusters have been reported, however the clusters of the highest nuclearities are hexanuclear species: $[Ir_2Ru_4B(CO)_{16}]^{2-}$ and its triphenylphosphine gold derivative $[Ir_2Ru_4B(CO)_{16}(AuPPh_3)]^-$.[14] In this paper we report the syntheses of novel high-nuclearity IrRu clusters with capping $\{Ru(CO)_3\}$ groups.

Results and discussion

Synthesis of $[PPh_4][Ir_7Ru_3(CO)_{23}]$ 1

A solution of $[PPh_4]_2[Ir_6(CO)_{15}]$ and $[Ru_3(CO)_{12}]$ in diglyme was refluxed (161 °C) under argon and after 4 h no starting material, $[PPh_4]_2[Ir_6(CO)_{15}]$, was observed by IR. When the $[N(PPh_3)_2]^+$

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Table 1 Selected bond lengths (Å) for $[N\{P(C_6H_4Me\text{-}p)_3\}_2][Ir_7Ru_3(CO)_{23}]$ **1a**

Ir1–Ir2	2.761(1)	Ir3–Ru3	2.742(2)
Ir1–Ir3	2.752(1)	Ir4–Ir5	2.719(1)
Ir1–Ir4	2.757(1)	Ir4–Ir6	2.736(1)
Ir1–Ir5	2.766(1)	Ir4–Ru1	2.761(2)
Ir1–Ir7	2.939(1)	Ir4–Ru3	2.742(2)
Ir1–Ru1	2.699(2)	Ir5–Ir6	2.727(1)
Ir2–Ir3	2.735(1)	Ir5–Ru1	2.758(2)
Ir2–Ir5	2.740(1)	Ir5–Ru2	2.753(2)
Ir2–Ir6	2.738(1)	Ir6–Ru2	2.767(2)
Ir2–Ir7	2.721(1)	Ir6–Ru3	2.760(2)
Ir2–Ru2	2.730(2)	Ir–C (mean)	1.854(11)
Ir3–Ir4	2.738(1)	Ru–C (mean)	1.878(7)
Ir3–Ir6	2.736(1)	IrO–C (mean)	1.154(6)
Ir3–Ir7	2.704(1)	RuO–C (mean)	1.151(9)

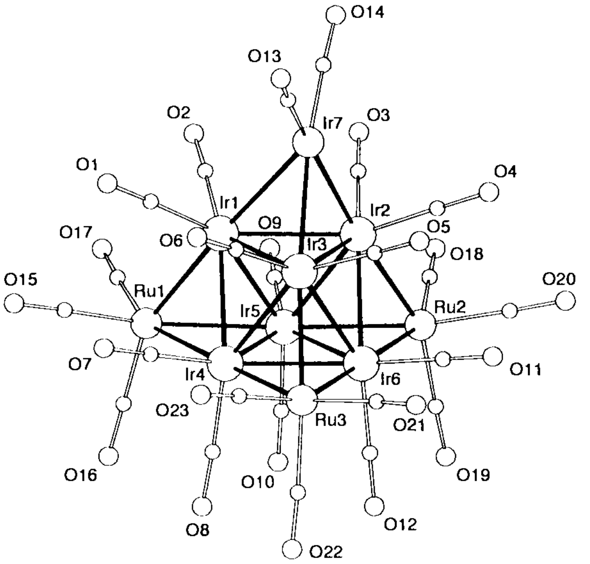

Fig. 1 Anion structure of $[N\{P(C_6H_4Me\text{-}p)_3\}_2][Ir_7Ru_3(CO)_{23}]$ **1a** with labelling of selected atoms; carbon atoms have the same digit as the oxygen atoms to which they are bonded.

or $[N\{P(C_6H_4Me\text{-}p)_3\}_2]^+$ salt of $[Ir_6(CO)_{15}]^{2-}$ was employed as the starting material the reaction time decreased to 2 or 1 h, respectively, suggesting that the higher acidity of the counter cation increased the reactivity. IR and X-ray analysis confirmed that the anionic products of the cluster complexes were identical. The yields of the cluster anion were consistent with the relative reactivity series of the counter cation, that is $[N\{P(C_6H_4Me\text{-}p)_3\}_2]^+ > [N(PPh_3)_2]^+ > [PPh_4]^+$. The effect of proton addition was examined. In the presence of an equimolar amount of *p*-toluenesulfonic acid the reaction between $[PPh_4]_2[Ir_6(CO)_{15}]$ and $[Ru_3(CO)_{12}]$ was completed after 1 h heating at 120 °C. The main product was purified by crystallization and analysed by X-ray diffraction.

The cluster was formulated as $[PPh_4][Ir_7Ru_3(CO)_{23}]$ **1**, but the single crystals of the $[PPh_4]^+$ salt were very thin plates which were difficult fully to characterize. In order to obtain better single crystals for X-ray analysis the $[N(PPh_3)_2]^+$ and $[N\{P(C_6H_4Me\text{-}p)_3\}_2]^+$ salts were prepared. Well grown thick single crystals of the latter were obtained and successfully characterized by X-ray crystallography. The molecular structure of the cluster anion of $[N\{P(C_6H_4Me\text{-}p)_3\}_2][Ir_7Ru_3(CO)_{23}]$ **1a** is shown in Fig. 1 and selected bond lengths are given in Table 1. The cluster is a monoanion with a tetracapped octahedral metal framework, which represents a rare example of a heteronuclear IrRu cluster. The overall metal structure is identical to those of $[Ru_{10}C(CO)_{24}]^{2-}$, $[Ru_{10}N(CO)_{24}]^-$ and $[Os_{10}C(CO)_{24}]^{2-}$ containing 134 cluster valence electrons. Of the four capping metal atoms, three are ruthenium and the fourth, quite unexpectedly, is iridium. The assignment was confirmed by chemical analysis and crystal structure determination. All the carbonyl ligands are terminally bonded and essentially linear.

The cluster is a monoanion so it cannot be formulated as $[Ir_6Ru_4(CO)_{23}]^{2-}$, which corresponds to the simple addition product of four $\{Ru(CO)_3\}$ groups to the Ir_6 metal core. No resonance characteristic for an M–H linkage was detected in the ^1H NMR spectrum of **1** (δ −100 to +100) and no reaction was observed with $[OH]^-$. Thus **1** is not a protonated product formulated as $[Ir_6Ru_4H(CO)_{23}]^-$ with four tetrahedrally capping ruthenium atoms and 134 valence electrons, which we initially assumed. Twentyfour carbonyl ligands are necessary for the assignment of two carbonyl groups to each iridium atom and three to each ruthenium atom of $[Ir_6Ru_4(CO)_{23}]^{2-}$ or $[Ir_6Ru_4H(CO)_{23}]^-$, provided that there are no bridging carbonyl groups. All the known anionic and neutral decanuclear carbonyl clusters of the same metal framework have only terminally co-ordinated carbonyl ligands and no bridging carbonyl ligands have been reported.[4–6,8–10,15] From the isotope shift of the Mössbauer spectrum of $[N(PPh_3)_2]_2[Ru_{10}C(CO)_{24}]$ at 5 K the state of the ruthenium atoms has been revealed to be essentially neutral,[16] which shows that the negative charges are located not on the ruthenium atoms but on the CO ligands. Strong electron-withdrawing groups such as bridging or capping CO ligands are not appropriate for such high-nuclearity complexes. Consequently, cluster **1** was produced by incorporation of the capping $\{Ir(CO)_2\}^+$ moiety to avoid the deficiency in the number of terminally bound carbonyl ligands.

The effect of the addition of *p*-toluenesulfonic acid was examined. Product **1** was fairly stable, and was quantitatively recovered after treatment with an equimolar amount of *p*-toluenesulfonic acid at reflux temperature in diglyme for 1 h. One third of $[PPh_4]_2[Ir_6(CO)_{15}]$ was decomposed by heating at 120 °C for 1 h in the presence of *p*-toluenesulfonic acid in diglyme and practically all was decomposed by heating at 140 °C for 30 min, whereas in the absence of the acid no breakdown was detected after refluxing for 4 h in diglyme. Consequently, protonation served to decompose the $[Ir_6(CO)_{15}]^{2-}$ to produce $\{Ir(CO)_2\}^+$, in accordance with the different reactivity of the counter cations of $[Ir_6(CO)_{15}]^{2-}$.

X-Ray studies of compound **1a** confirmed that the Ir_6 unit has remained intact in the reaction with $[Ru_3(CO)_{12}]$. As shown in Table 1, the Ir–Ir bond lengths in the octahedron range from 2.719(1) to 2.766(1) Å (average 2.742(4) Å). The corresponding bond lengths in the parent molecule $[Ir_6(CO)_{15}]^{2-}$ and in the neutral cluster $[Ir_6(CO)_{16}]$ are in the ranges 2.730(1)–2.822(1) (mean 2.773(8))[13] and 2.743(2)–2.810(2) (mean 2.779 Å),[17] respectively. The octahedron shrank slightly upon capping by $\{Ru(CO)_3\}$ and $\{Ir(CO)_2\}$ groups as was also observed in the formation of $[Ru_{10}C(CO)_{24}]^{2-}$[10] from $[Ru_6C(CO)_{16}]^{2-}$.[18,19] The capping $\{Ir(CO)_2\}$ group is asymmetric with one long (2.939(1) Å) and two short bonds (2.721(1) and 2.704(1) Å) to the central octahedron. Two kinds of triply bridging iridium–carbonyl groups that are co-ordinated to the octahedral iridium metal framework have been reported: $\{Ir(CO)_3\}$ in $[Ir_{14}(CO)_{27}]^-$[20] and $\{Ir(CO)_2\}$ in $[Ir_{12}(CO)_{24}]^{2-}$.[21] The former is a symmetrical cap with Ir–Ir distances in the range 2.674(1)–2.681(1) Å, and the latter is an asymmetric cap with a longer Ir–Ir distance of 2.939(1) Å and shorter distances of 2.672(1) and 2.654(1) Å. Similar to the latter case, the capping atom Ir7 in **1a** adopts an almost square planar co-ordination with respect to its two terminal carbonyl ligands and iridium atoms (Ir2 and Ir3) and interacts weakly with the axial Ir1.

There have been no examples of a Ru metal atom capping a triangular face of iridium. The capping Ru–Ir distances in compound **1a** (mean 2.746(7) Å) are substantially equal to the corresponding capping Ru–Ru distances in the structurally similar clusters $[Ru_{10}C(CO)_{24}]^{2-}$ (mean 2.769(4) Å) but slightly shorter than those in $[Ru_{10}N(CO)_{24}]^-$ (mean 2.788(3) Å). All the carbonyls in **1a** are terminal: two are connected to each iridium atom and three to each ruthenium atom with bonding param-

Table 2 Selected bond lengths (Å) for $[Ir_7Ru_3(CO)_{23}(AuPPh_3)]$ **2**

Au–Ir7	2.620(2)	Ir3–Ir7	2.699(1)
Au–P	2.269(8)	Ir3–Ru3	2.757(2)
Ir1–Ir2	2.745(1)	Ir4–Ir5	2.721(1)
Ir1–Ir3	2.752(1)	Ir4–Ir6	2.726(1)
Ir1–Ir4	2.741(1)	Ir4–Ru1	2.765(2)
Ir1–Ir5	2.754(2)	Ir4–Ru3	2.746(2)
Ir1–Ir7	2.844(1)	Ir5–Ir6	2.733(1)
Ir1–Ru1	2.701(2)	Ir5–Ru1	2.755(2)
Ir2–Ir3	2.724(1)	Ir5–Ru2	2.753(2)
Ir2–Ir5	2.741(1)	Ir6–Ru2	2.757(2)
Ir2–Ir6	2.741(1)	Ir6–Ru3	2.770(2)
Ir2–Ir7	2.729(2)	Ir–C (mean)	1.899(11)
Ir2–Ru2	2.754(3)	Ru–C (mean)	1.896(10)
Ir3–Ir4	2.738(1)	IrO–C (mean)	1.131(9)
Ir3–Ir6	2.731(2)	RuO–C (mean)	1.124(16)

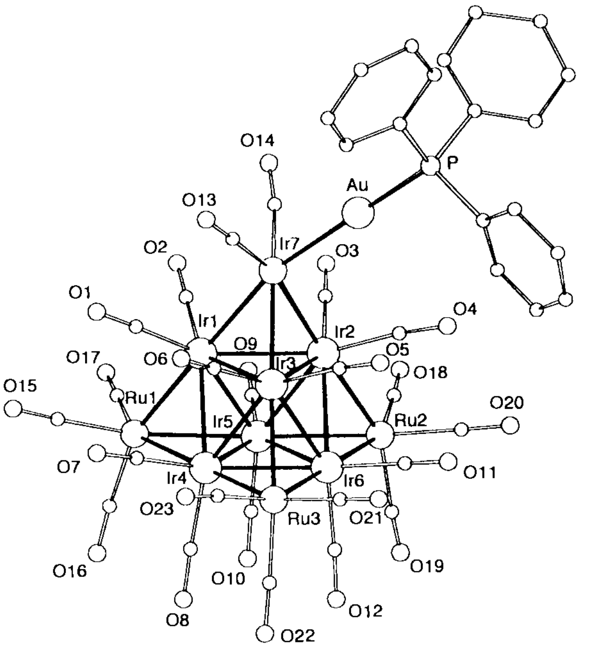

Fig. 2 Structure of $[Ir_7Ru_3(CO)_{23}(AuPPh_3)]$ **2**. Details as in Fig. 1.

eters corresponding to those of normal iridium or ruthenium carbonyl cluster complexes, respectively.

Synthesis of $[Ir_7Ru_3(CO)_{23}(AuPPh_3)]$ 2

Cluster **1** was allowed to react with $[AuCl(PPh_3)]$ in the presence of $AgOSO_2CF_3$ at room temperature. The reaction proceeded immediately to produce a neutral cluster. The IR spectrum of the product exhibits bands similar to those of **1**, but shifted *ca.* 13 cm^{-1} to higher wavenumber, consistent with the normal addition of the electrophilic gold fragment $\{AuPPh_3\}^+$ to a parent cluster. The structure of the product $[Ir_7Ru_3(CO)_{23}(AuPPh_3)]$ **2** is shown in Fig. 2 and selected bond lengths are presented in Table 2. The metal skeleton as well as the terminal carbonyl group stereochemistry in **2** is practically identical with that of **1a**. Formally, addition of $\{AuPPh_3\}^+$ to the less hindered apical iridium atom of **1** yielded **2**. One of the common metal–gold bond linkages is linear, as in Ir–Au dinuclear complexes. However, there are no precedents of gold ligands terminally co-ordinating to an iridium atom in cluster complexes. The Ir–Au bond (2.620(2) Å) is markedly shorter than the corresponding bonds (2.6569(6) to 3.007(3) Å) in complexes where the gold atoms serve as bridging or face-capping ligands: $[Ir_4(CO)_{10}(PPh_2)(\mu\text{-}AuPPh_3)]$,[22] $[Ir_4(CO)_{11}(PhPPPh)Ir_4(CO)_9(\mu_3\text{-}AuPEt_3)(\mu_4\text{-}AuPEt_3)]$,[23] $[Ir_6(CO)_{15}(\mu_3\text{-}AuPPh_3)]^-$[24] and $[Ir_6(CO)_{15}(\mu\text{-}AuPPh_3)(\mu_4\text{-}AuPPh_3)]$.[25]

There are no significant differences between the Ir–Ir and Ir–Ru bond lengths in the metal cores of compounds **1a** and **2** (Tables 1 and 2). On the other hand, the metal–carbon distances of the terminal carbonyl ligands in **2** (mean 1.898(8) Å) are longer than in **1a** (mean 1.863(7) Å), and the C–O distances in **2** (mean 1.128(8) Å) are shorter than the corresponding distances in **1a** (mean 1.153(4) Å). Neutralization of the negative charge in **1a** by addition of $\{AuPPh_3\}^+$ caused the decrease of metal–carbonyl back bonding interactions.

Table 3 Selected bond lengths (Å) for $[PPh_4][Ir_6Ru_3(CO)_{21}(AuPPh_3)]$ **3**

Au–Ir1	2.826(3)	Ir3–Ru3	2.702(4)
Au–Ir2	2.812(2)	Ir4–Ir5	2.730(3)
Au–Ir3	2.857(2)	Ir4–Ir6	2.718(3)
Au–P1	2.22(1)	Ir4–Ru1	2.755(6)
Ir1–Ir2	2.771(3)	Ir4–Ru3	2.747(6)
Ir1–Ir3	2.773(4)	Ir5–Ir6	2.724(4)
Ir1–Ir4	2.753(2)	Ir5–Ru1	2.755(5)
Ir1–Ir5	2.767(2)	Ir5–Ru2	2.771(5)
Ir1–Ru1	2.696(5)	Ir6–Ru2	2.762(4)
Ir2–Ir3	2.750(3)	Ir6–Ru3	2.759(4)
Ir2–Ir5	2.766(3)	Ir–C (mean)	1.83(3)
Ir2–Ir6	2.773(2)	Ru–C (mean)	1.87(3)
Ir2–Ru2	2.680(4)	IrO–C (mean)	1.19(3)
Ir3–Ir4	2.763(3)	RuO–C (mean)	1.17(3)
Ir3–Ir6	2.762(2)		

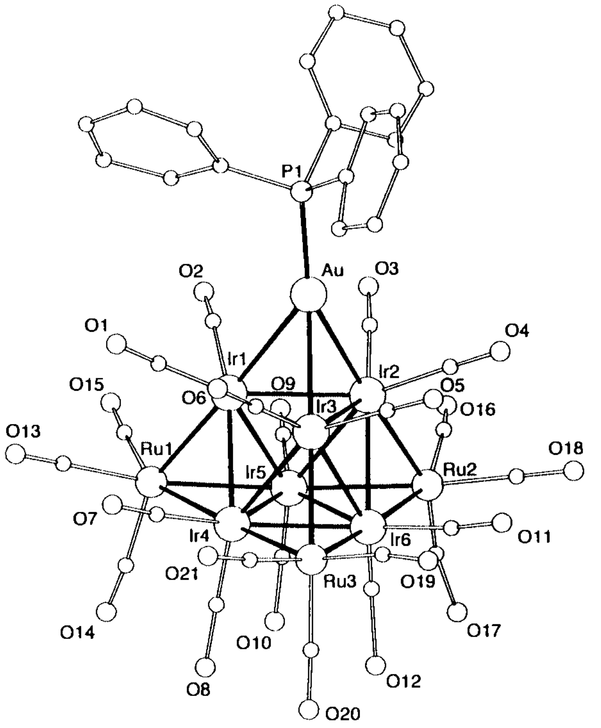

Fig. 3 Anion structure of $[PPh_4][Ir_6Ru_3(CO)_{21}(AuPPh_3)]$ **3**. Details as in Fig. 1.

Synthesis of $[PPh_4][Ir_6Ru_3(CO)_{21}(AuPPh_3)]$ 3

A solution of compound **1** and $[AuCl(PPh_3)]$ in 1,2-dichloroethane was refluxed for 3 h until the $\nu(C=O)$ bands characteristic for **1** disappeared. After chromatographic purification followed by crystallization the main product was isolated. The pattern of the $\nu(C=O)$ absorption bands is similar to that of **1**. However, each band is shifted by *ca.* 14 cm^{-1} to lower energy, which indicates that the electron density on the metals has increased. The structure of the product was confirmed by X-ray single-crystal analysis. The molecular structure of the cluster anion is shown in Fig. 3 and the selected bond lengths are listed in Table 3. The product cluster $[PPh_4][Ir_6Ru_3(CO)_{21}(AuPPh_3)]$ **3** was formed by replacement of the capping $\{Ir(CO)_2\}^+$ group in **1** with $\{AuPPh_3\}^+$. In the reported reaction of $[Pt_6(\mu\text{-}CO)_6(\mu\text{-}dppm)_3]$ (dppm = $Ph_2PCH_2PPh_2$) with $[Ir(CO)_4]^-$ that gives $[Pt_6(\mu\text{-}CO)_6(\mu\text{-}dppm)_3\{\mu_3\text{-}Ir(CO)_2\}]$, the reagent acted as a

Table 4 Crystallographic data for compounds **1a**, **2** and **3**

	$[N\{P(C_6H_4Me\text{-}p)_3\}_2][Ir_7Ru_3(CO)_{23}]$	$[Ir_7Ru_3(CO)_{23}(AuPPh_3)]\cdot 2CH_2Cl_2$	$[PPh_4][Ir_6Ru_3(CO)_{21}(AuPPh_3)]$
Chemical formula	$C_{42}H_{42}NP_2\cdot C_{23}Ir_7O_{23}Ru_3$	$C_{41}H_{15}AuIr_7O_{23}PRu_3\cdot C_2H_4Cl_4$	$C_{24}H_{20}P\cdot C_{39}H_{15}AuIr_6O_{21}PRu_3$
Formula weight	2915.74	2922.11	2843.40
Crystal system	Triclinic	Monoclinic	Triclinic
Space group (no.)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	15.898(2)	17.271(2)	16.819(9)
b/Å	22.118(2)	17.957(4)	17.188(4)
c/Å	11.950(1)	21.029(3)	16.321(3)
α/°	94.89(2)		110.74(2)
β/°	96.11(1)	111.525(10)	112.47(3)
γ/°	105.50(2)		64.29(4)
U/Å^3	3997.7(9)	6067(2)	3827(3)
T/°C	21	21	21
Z	2	4	2
μ/cm^{-1} (Mo-Kα)	122.89	187.43	130.12
Measured reflections	15446	12874	12393
Unique observed reflections	8020	8028	5688
Final R (R')	0.042 (0.048)	0.051 (0.054)	0.064 (0.069)

source of $\{Ir(CO)_2\}^-$, which serves as a 2-electron ligand. Comparison of $[Pt_6(\mu\text{-}CO)_6(\mu\text{-}dppm)_3(\mu_3\text{-}AuPPh_3)_2]$ with $[Pt_6(\mu\text{-}CO)_6(\mu\text{-}dppm)_3\{\mu_3\text{-}Ir(CO)_2\}(\mu_3\text{-}AuPPh_3)]$ suggests that the $\{Ir(CO)_2\}^+$ group is isolobal with $\{AuPPh_3\}^+$ even though the latter complex has not fully been characterized.[26] In this study comparison of **1a** and **3** clearly shows that the $\{Ir(CO_2)\}^+$ group, originating from decomposition of $[Ir_6(CO)_{15}]^{2-}$ by protonation, is isolobal with the $\{AuPPh_3\}^+$ group. Note that the electron count used is for the Ir_6Ru_3 unit only, counting either the $\{Ir(CO)_2\}^+$ or $\{AuPPh_3\}^+$ units as a 0-electron ligand. This treatment is appropriate since the similarity in structures of the Ir_6Ru_3 cores in **1a** and **3** is then emphasized, but it is also possible to consider the adducts as decanuclear clusters and then **1a** and **3** are not strictly isoelectronic.

The monoanion **3** exhibits an approximate C_3 symmetry. There is little asymmetry in the capping mode of $AuPPh_3$ as indicated by the 2.812(2)–2.857(2) Å Ir–Au distances in **3**, which are in the expected range for Ir–Au single bonds as mentioned above. There are no significant differences between Ir–Ir and Ir–Ru bond lengths in complexes **1a** and **3**.

The metal core of compound **3** may be viewed as being derived by addition of a capping $\{AuPPh_3\}^+$ group to the Ir_6Ru_3 metal framework in $[Ir_6Ru_3(CO)_{21}]^{2-}$, which is assumed to have 122 valence electrons. On the other hand, the corresponding osmium cluster complex $[Os_9H(CO)_{24}]^-$ with a tricapped octahedral metal core has been reported.[27] The three Ru atoms in **3** lie below the plane defined by Ir1, Ir2 and Ir3 with an average deviation of 0.089 Å. For $[Os_9H(CO)_{24}]^-$ there is an average deviation of 0.30 Å from the corresponding plane. This feature is not observed in **1a** and **2**, where the corresponding values are −0.037 and −0.021 Å, respectively.

Experimental

General procedures

The compounds $[N\{P(C_6H_4Me\text{-}p)_3\}_2]Cl$,[28] $[PPh_4]_2[Ir_6(CO)_{15}]$[29] and $[AuCl(PPh_3)]$[30] were prepared according to the published procedures. The complexes $[N\{P(C_6H_4Me\text{-}p)_3\}_2]_2\ [Ir_6(CO)_{15}]$ and $[N(PPh_3)]_2[Ir_6(CO)_{15}]$ were prepared using $[N\{P(C_6H_4\text{-}Me\text{-}p)_3\}_2]Cl$ and $[N(PPh_3)_2]Cl$ instead of $[PPh_4]Br$. The solvents used for the reactions, CH_2Cl_2, CH_2ClCH_2Cl and bis(2-methoxyethyl) ether, were distilled over phosphorus pentaoxide or sodium under argon. Solvents used for purification were used as received. All the reactions and crystallization procedures were carried out under an atmosphere of purified argon. Other procedures were promptly performed under the ambient atmosphere because the products were moderately air-stable in solution as well as in the solid state. IR and NMR spectra were measured with a Perkin-Elmer FT1600 spectrophotometer and a JEOL RX-270 spectrometer, respectively, FAB-MS spectra with a JEOL JMS-HX 110A double-focusing spectrometer using *m*-nitrobenzyl alcohol as a liquid matrix.

Syntheses

$[PPh_4][Ir_7Ru_3(CO)_{23}]$ 1. An ethanol solution of *p*-toluenesulfonic acid monohydrate (42 mg, 0.22 mmol in 0.22 cm^3 ethanol) was added to a flask containing $[PPh_4]_2[Ir_6(CO)_{15}]$ (0.500 g, 0.222 mmol) and $[Ru_3(CO)_{12}]$ (0.185 mg, 0.289 mmol) and evaporated to dryness. After addition of diglyme (15 cm^3) the suspension was heated in an oil-bath at 120 °C for 1 h during which time the solid disappeared and the solution changed from brown to deep green. After reduction of the solvent *in vacuo* followed by the addition of CH_2Cl_2 (10 cm^3), the solution was filtered to remove insoluble materials. Hexane (2 cm^3) was slowly added and partial reduction of the solvent gave a deep green crystalline product (0.459 mg, 90% yield based on $[PPh_4]_2[Ir_6(CO)_{15}]$), $\tilde{\nu}_{max}$/cm^{-1} (CO) 2089w, 2051vs, 2035s and 2021m (CH_2Cl_2).

$[N\{P(C_6H_4Me\text{-}p)_3\}_2][Ir_7Ru_3(CO)_{23}]$ **1a** was obtained in the same way from $[N\{P(C_6H_4Me\text{-}p)_3\}_2]_2[Ir_6(CO)_{15}]$ (Found: C, 27.31; H, 1.84; Ir, 45.25; N, 0.47; Ru, 10.68. $C_{65}H_{42}Ir_7NO_{23}P_2Ru_3$ requires C, 26.78; H, 1.45; Ir, 46.15; N, 0.48; Ru, 10.40%); $\tilde{\nu}_{max}$/cm^{-1} (CO) 2089w, 2051vs, 2035s and 2021m (CH_2Cl_2). Clusters **1** and **1a** can be purified by cellulose column chromatography when necessary.

$[Ir_7Ru_3(CO)_{23}(AuPPh_3)]$ 2. CH_2Cl_2 (6 cm^3) was added to a flask containing $[AuCl(PPh_3)]$ (72 mg, 0.146 mmol) and $AgOSO_2CF_3$ (27 mg, 0.105 mmol). Then the fine white precipitate was removed by filtration. $[PPh_4][Ir_7Ru_3(CO)_{23}]$ (251 mg, 0.095 mmol) was added to the filtrate with stirring and immediately the deep green solution turned green. The solution was evaporated to dryness under vacuum and the product purified by column chromatography on silica gel (10% water, 2.5 cm i.d. × 20 cm). A green band eluted with hexane–CH_2Cl_2 (9:1) was collected and the solvent evaporated to dryness. Recrystallization of the residue from CH_2Cl_2–hexane yielded deep green crystals (93 mg, 36%) (Found: C, 18.31; H, 0.67. $C_{41}H_{15}AuIr_7O_{23}PRu_3$ requires C, 17.89; H, 0.55%); $\tilde{\nu}_{max}$/cm^{-1} (CO) 2097w, 2065vs, 2047s and 2034m (CH_2Cl_2).

$[PPh_4][Ir_6Ru_3(CO)_{21}(AuPPh_3)]$ 3. A solution of $[PPh_4][Ir_7Ru_3(CO)_{23}]$ (204 mg, 0.077 mmol) and $[AuCl(PPh_3)]$ (109 mg, 0.22 mmol) in CH_2ClCH_2Cl (12 cm^3) was refluxed for 3 h. The deep green solution turned dark. Concentration of the solution followed by separation by column chromatography on 15% water-containing silica gel (hexane–CH_2Cl_2, 1 : 3) gave the green band of the product. Slow evaporation of the solvent yielded deep green crystals (72 mg, 32%) ([N{P(C_6H_4Me-*p*)$_3$}$_2$] salt, Found: C, 27.38; H, 1.72. $C_{67}H_{43}AuIr_6O_{21}P_2Ru_3$ requires C, 27.75; H, 1.49%); $\tilde{\nu}_{max}$/cm^{-1} (CO) 2076w, 2038vs, 2020s, and 2006m (sh) (CH_2Cl_2); *m*/*z* 2504 ([$Ir_6Ru_3(CO)_{21}AuPPh_3$]$^+$).

Structure determinations

Black single crystals of compound **1a** were grown by diffusion of hexane into a CH_2Cl_2 solution in a glass tube (internal diameter 8 mm) at ambient temperature. Deep green single crystals of **2** and **3** were obtained by slow evaporation of the solvent from CH_2Cl_2–hexane solutions. Crystals were fixed on the tip of a glass fibre with cyanoacrylate adhesive. Intensity data were collected on a Rigaku RAXIS CS Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation. Crystallographic data are given in Table 4. As refinement proceeded the tolyl groups of **1a** and phenyl groups of **3** in the counter cation were treated as rigid groups. Cluster **2** crystallized with two molecules of CH_2Cl_2 in the asymmetric crystal unit. In **1a** and **2** treatment of all four capping metals as ruthenium led to marginally higher residuals and abnormally low thermal parameters for one of the atoms, while treatment of the atom as iridium led to appropriate final data.

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See http://www.rsc.org/suppdata/dt/b0/b003100n/ for crystallographic files in .cif format.

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