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The mixed-metal carbonyl cluster anion $[Ru_3Ir(CO)_{13}]^-$: synthesis, molecular structure, fluxionality, reactivity †

Georg Süss-Fink,* Susanne Haak, Vincent Ferrand and Helen Stoeckli-Evans

Institut de Chemie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

The new cluster anion $[Ru_3Ir(CO)_{13}]^-$ **1** was synthesized in high yield from $[Ru_3(CO)_{12}]$ and $[Ir(CO)_4]^-$. The single-crystal X-ray structure analysis of the bis(triphenylphosphoranylidene)ammonium salt revealed the presence of two isomers, $[Ru_3Ir(CO)_{11}(\mu\text{-}CO)_2]^-$ **1a** and $Ru_3Ir(CO)_9(\mu\text{-}CO)_4]^-$ **1b** in the same crystal. Both **1a** and **1b** present a tetrahedral Ru_3Ir framework, differing only by the number of bridging carbonyl ligands. Variable-temperature ^{13}C NMR spectroscopic studies of **1** revealed the fluxionality of the carbonyl ligands and the interconversion of both isomers in solution. Protonation of **1** gave the neutral cluster $[HRu_3Ir(CO)_{13}]$ **2**, whereas reaction of **1** with molecular hydrogen yielded the anion $[H_2Ru_3Ir(CO)_{12}]^-$ **3**. Either hydrogenation of **2** or protonation of **3** gave $[H_3Ru_3Ir(CO)_{12}]$ **4**. The tetrahedral structure of the hydrido derivatives was confirmed by a single-crystal X-ray structure analysis of the bis(triphenylphosphoranylidene)ammonium salt of **3**.

The chemistry of mixed-metal clusters[1] has received much attention because of the catalytic potential of these complexes.[2] The concept of cluster catalysis is based on the idea that catalytic transformations of a substrate may require co-ordination to several metal atoms of the cluster framework.[3] Different metals in a cluster may have synergistic effects for a catalytic transformation. The dramatic increase in the catalytic activity of a transition-metal complex by the addition of another metal compound always gives rise to speculation about the formation of highly active mixed-metal species to account for the synergistic effect observed.[4]

In a recent patent[5] it was shown that the carbonylation of methanol to give acetic acid is effectivly catalysed by various iridium complexes, especially when promoted by ruthenium compounds. Excellent results were obtained for a ruthenium–iridium ratio of 3 : 1.[5] These findings prompted us to investigate Ru_3Ir carbonyl clusters, which seem to be missing links in the series of tetranuclear mixed-metal clusters. Whereas the cluster anions $[Ru_3Co(CO)_{13}]^-$ [6] and $[Os_3Co(CO)_{13}]^-$ [7] have been known since 1980 from the reaction of $[Co(CO)_4]^-$ with $[M_3(CO)_{12}]$ (M = Ru or Os), the analogous reaction of $[Rh(CO)_4]^-$ with $[Ru_3(CO)_{12}]$ did not give the expected $[Ru_3Rh(CO)_{13}]^-$ cluster anion, but instead $[Ru_2Rh_2(CO)_{12}]^{2-}$.[8] In the case of Ru_3Ir clusters, no homoleptic carbonyl anion has been reported so far.

In this paper we describe the synthesis and structure of the 'missing' cluster anion $[Ru_3Ir(CO)_{13}]^-$ and its protonation and hydrogenation reactions to give the hydrido derivatives $[HRu_3Ir(CO)_{13}]$, $[H_2Ru_3Ir(CO)_{12}]^-$ and $[H_3Ru_3Ir(CO)_{12}]$. Studies on the catalytic activity of the Ru_3Ir clusters for carbonylation reactions are underway.

Results and Discussion

Synthesis and characterization of $[Ru_3Ir(CO)_{13}]^-$

The reaction of the anion $[Ir(CO)_4]^-$ with $[Ru_3(CO)_{12}]$ in tetrahydrofuran (thf) solution under refluxing conditions leads to the mixed-metal cluster anion $[Ru_3Ir(CO)_{13}]^-$ **1** which was isolated almost quantitatively as the bis(triphenylphosphoranylidene)ammonium salt from a diethyl ether–hexane mixture [equation (1)]. The product is obtained as a red-brown microcrystalline powder; it appears to be stable towards air and moisture even during long periods. The compound is soluble only in polar organic solvents such as diethyl ether, thf, dichloromethane or methanol. The IR spectrum of **1** presents, similarly to the analogous $[Ru_3Co(CO)_{13}]^-$,[6] four vibrations in the region of the terminal carbonyl ligands and two absorptions which are attributed to the bridging carbonyl groups (Table 1). In the ^1H NMR spectrum only one signal (multiplet) centred at δ 7.55 is observed, which can be assigned to the $[N(PPh_3)_2]^+$ cation.

$$[Ru_3(CO)_{12}] + [Ir(CO)_4]^- \longrightarrow [Ru_3Ir(CO)_{13}]^- + 3\ CO \quad (1)$$

† *Non-Si unit employed*: bar = 10^5 Pa.

Solid-state structure and fluxionality of $[Ru_3Ir(CO)_{13}]^-$

The crystal-structure analysis of $[N(PPh_3)_2][Ru_3Ir(CO)_{13}]$ revealed three independent anionic molecules per asymmetric unit of the unit cell, which is due to the high intramolecular mobility of the carbonyl ligands. The crystal consists of discrete $[N(PPh_3)_2]^+$ cations and $[Ru_3Ir(CO)_{13}]^-$ anions, showing normal intermolecular contacts between the atoms of the ions. In two of the three different anions the co-ordination of the carbonyl ligands is the same, with two bridging and eleven terminal carbonyls, $[Ru_3Ir(\mu\text{-}CO)_2(CO)_{11}]^-$ **1a**, whereas the third molecule represents an isomer with four bridging and nine terminal CO groups, $[Ru_3Ir(\mu\text{-}CO)_4(CO)_9]^-$ **1b**. This is in contrast to the known isoelectronic cluster $[Ru_3Co(CO)_{13}]^-$, which contains three bridging and ten terminal CO groups.[6] The structures of one of the two molecules of isomer **1a** and that of isomer **1b** are depicted in Figs. 1 and 2, respectively; selected bond distances and angles are given in Tables 2 and 3, respectively.

The structure of **1a** is described for only one of the two independent molecules. The second molecule presents the same co-ordination and similar bond lengths and angles, see Table 2. The Ru_3Ir core of **1a** defines an almost regular tetrahedron, the Ru–Ir distances being approximately the same (average 2.75 Å), which compares well with the Ru–Ir bond distances in the known hydrido complexes $[H_2Ru_3Ir(CO)_{12}Cl]$[9] and $[H_3Ru_3Ir(CO)_{11}(PPh_3)]$.[10] The three Ru–Ru bonds are all different, the Ru(4)–Ru(5) [2.766(2) Å] and Ru(4)–Ru(6) [2.752(2) Å] bonds being bridged by a μ_2-carbonyl ligand and therefore being shorter than the non-bridged Ru(5)–Ru(6) edge [2.811(2) Å]. Of the eleven terminal carbonyl ligands, two are bound to Ru(4), three to Ru(5), three to Ru(6) and three to the Ir atom. Whereas the μ-CO bridge of the Ru(4)–Ru(5) bond is distinctly asymmetrical [Ru(4)–C(57) 1.94(2), Ru(5)–C(57) 2.50(2) Å], thus representing a semi-bridging carbonyl, the asymmetry of

Table 1 Infrared and ^{1}H NMR spectroscopy data

	Complex	IR ν(CO) [a]/cm^{-1}	^{1}H NMR [b]
$[N(PPh_3)_2]$ **1**	$[N(PPh_3)_2][Ru_3Ir(CO)_{13}]$	2068w, 2017vs, 1970s, 1924w, 1821m, 1803m	7.40–7.70 (30 H, m)
2	$[HRu_3Ir(CO)_{13}]$	2074s, 2057vs, 2018w (sh), 1874w (br)	−17.93 (1 H, s)
$[N(PPh_3)_2]$ **3**	$[N(PPh_3)_2][H_2Ru_3Ir(CO)_{12}]$	2074w, 2038s, 2005vs, 1968m, 1952m, 1819w, 1805m	−20.64 (2 H, s), 7.40–7.70 (30 H, m)
4	$[H_3Ru_3Ir(CO)_{12}]$	2079vs, 2054s, 2033m, 2023m	−17.93 (3 H, s)

[a] Recorded in diethyl ether (**1**), dichloromethane (**2**), thf (**3**) or hexane (**4**) solution. [b] Measured in $CDCl_3$ solution at 294 K, data given as chemical shift (δ) (relative intensity, multiplicity).

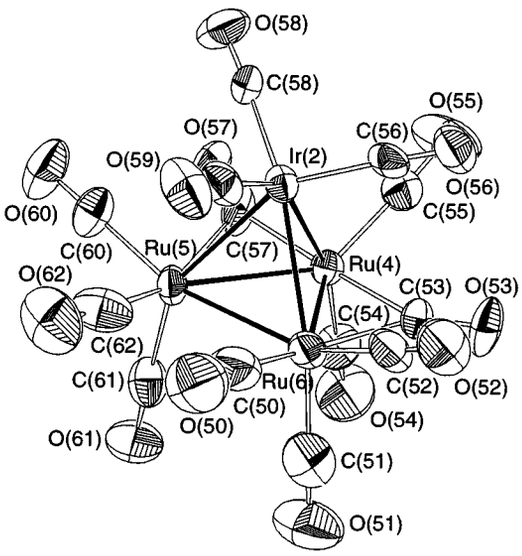


Fig. 1 Molecular structure of cluster anion **1a**. The label for atom C(59) has been omitted for clarity

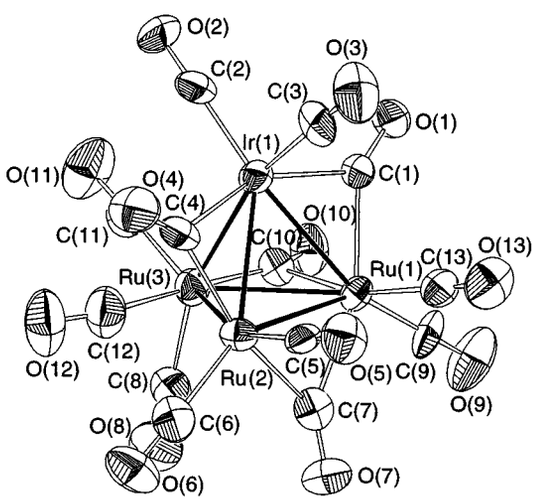


Fig. 2 Molecular structure of cluster anion **1b**

the μ-CO bridge across Ru(4)–Ru(6) is less pronounced [Ru(4)–C(53) 2.005(14), Ru(6)–C(53) 2.29(2) Å]. The C(53)–O(53) carbonyl bridge is almost co-planar with the ruthenium triangle, the Ru(6)–C(53)–Ru(4)–Ru(5) torsion angle being 1.0(5)°, whereas the C(57)–O(57) bridge lies out of the plane of the three ruthenium atoms; the torsion angle being 8.3(5)°.

In the tetrahedral Ru_3Ir core of isomer **1b**, not only the Ru–Ru bonds but also the Ru–Ir bonds are all different, due to the presence of four μ-CO bridges, two of which also involve the iridium atom. The atoms Ir(1), Ru(1) and Ru(2) carry two terminal CO groups each, while three terminal carbonyls are bound to Ru(3). Two Ru–Ir and two Ru–Ru edges are bridged by a μ-CO group, Ru(1) supporting three CO bridges, and

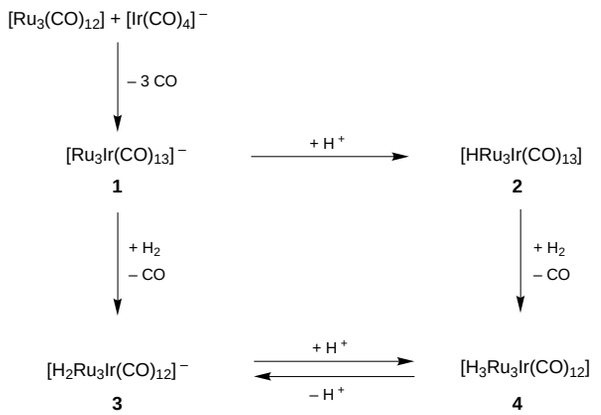
Table 2 Selected bond lengths (Å) and angles (°) for the molecules of anion **1a**

Molecule 1			
Ru(4)–Ru(5)	2.766(2)	Ir(2)–Ru(6)	2.742(2)
Ru(4)–Ru(6)	2.752(2)	Ru(4)–C(53)	2.005(14)
Ru(5)–Ru(6)	2.811(2)	Ru(4)–C(57)	1.94(2)
Ir(2)–Ru(4)	2.749(2)	Ru(5)–C(57)	2.50(2)
Ir(2)–Ru(5)	2.745(2)	Ru(6)–C(53)	2.29(2)
Ru(4)–Ru(5)–Ru(6)	59.13(6)	Ir(2)–Ru(5)–Ru(6)	59.12(6)
Ru(4)–Ru(6)–Ru(5)	59.62(5)	Ir(2)–Ru(6)–Ru(4)	60.05(5)
Ru(6)–Ru(4)–Ru(5)	61.26(6)	Ir(2)–Ru(6)–Ru(5)	59.24(5)
Ru(5)–Ir(2)–Ru(4)	60.45(5)	Ru(4)–C(53)–O(53)	147.8(12)
Ru(6)–Ir(2)–Ru(4)	60.16(5)	Ru(6)–C(53)–O(53)	132.3(10)
Ru(6)–Ir(2)–Ru(5)	61.64(6)	Ru(4)–C(53)–Ru(6)	79.3(5)
Ir(2)–Ru(4)–Ru(5)	59.70(5)	Ru(4)–C(57)–O(57)	153.0(13)
Ir(2)–Ru(4)–Ru(6)	59.79(5)	Ru(5)–C(57)–O(57)	131.1(11)
Ir(2)–Ru(5)–Ru(4)	59.84(5)	Ru(4)–C(57)–Ru(5)	75.9(6)
Molecule 2			
Ru(7)–Ru(8)	2.746(3)	Ir(3)–Ru(9)	2.738(2)
Ru(7)–Ru(9)	2.756(2)	Ru(7)–C(99)	1.96(2)
Ru(8)–Ru(9)	2.814(2)	Ru(7)–C(102)	2.02(2)
Ir(3)–Ru(7)	2.754(2)	Ru(8)–C(102)	2.39(2)
Ir(3)–Ru(8)	2.724(2)	Ru(9)–C(99)	2.46(2)
Ru(7)–Ru(8)–Ru(9)	59.40(6)	Ir(3)–Ru(8)–Ru(9)	59.23(5)
Ru(7)–Ru(9)–Ru(8)	59.07(6)	Ir(3)–Ru(9)–Ru(7)	60.17(5)
Ru(8)–Ru(7)–Ru(9)	61.53(5)	Ir(3)–Ru(9)–Ru(8)	58.75(5)
Ru(8)–Ir(3)–Ru(7)	60.16(6)	Ru(7)–C(99)–O(99)	151(2)
Ru(8)–Ir(3)–Ru(9)	62.02(5)	Ru(9)–C(99)–O(99)	152.3(14)
Ru(9)–Ir(3)–Ru(7)	60.23(5)	Ru(7)–C(99)–Ru(9)	76.3(7)
Ir(3)–Ru(7)–Ru(8)	59.38(6)	Ru(7)–C(102)–O(102)	153(2)
Ir(3)–Ru(7)–Ru(9)	59.60(5)	Ru(8)–C(102)–O(102)	130.2(14)
Ir(3)–Ru(8)–Ru(7)	60.46(5)	Ru(7)–C(102)–Ru(8)	76.6(7)

Table 3 Selected bond lengths (Å) and angles (°) for anion **1b**

Ru(1)–Ru(2)	2.736(2)	Ir(1)–C(1)	2.154(14)
Ru(1)–Ru(3)	2.895(2)	Ru(1)–C(7)	2.13(2)
Ru(2)–Ru(3)	2.863(2)	Ru(2)–C(7)	2.12(2)
Ir(1)–Ru(1)	2.743(2)	Ru(1)–C(10)	2.59(2)
Ir(1)–Ru(2)	2.749(2)	Ru(3)–C(10)	1.96(2)
Ir(1)–Ru(3)	2.809(2)	Ru(2)–C(4)	2.07(2)
Ru(1)–C(1)	2.060(14)	Ir(1)–C(4)	2.17(2)
Ru(1)–Ru(2)–Ru(3)	62.21(6)	Ru(1)–C(1)–O(1)	144.6(11)
Ru(2)–Ru(1)–Ru(3)	61.05(6)	Ir(1)–C(1)–O(1)	134.2(10)
Ru(2)–Ru(3)–Ru(1)	56.74(6)	Ru(1)–C(1)–Ir(1)	81.2(5)
Ru(1)–Ir(1)–Ru(2)	59.76(5)	Ru(1)–C(7)–O(7)	138.3(12)
Ru(1)–Ir(1)–Ru(3)	62.84(5)	Ru(2)–C(7)–O(7)	141.8(12)
Ru(2)–Ir(1)–Ru(3)	62.00(5)	Ru(1)–C(7)–Ru(2)	79.9(6)
Ru(1)–Ru(2)–Ir(1)	60.01(5)	Ru(1)–C(10)–O(10)	120.3(11)
Ru(2)–Ru(1)–Ir(1)	60.23(5)	Ru(3)–C(10)–O(10)	161.7(13)
Ir(1)–Ru(1)–Ru(3)	59.70(5)	Ru(1)–C(10)–Ru(3)	77.7(6)
Ir(1)–Ru(2)–Ru(3)	60.03(5)	Ru(2)–C(4)–O(4)	143.9(12)
Ir(1)–Ru(3)–Ru(1)	57.47(4)	Ir(1)–C(4)–O(4)	134.9(11)
Ir(1)–Ru(3)–Ru(2)	57.98(5)	Ru(2)–C(4)–Ir(1)	80.8(6)

Ru(2) two. The two carbonyl-bridged Ru–Ir edges are shorter (average 2.74 Å) than the non-bridged Ru(3)–Ir(1) bond which amounts to 2.809(2) Å, see Table 3. The carbonyl bridge across the atoms Ru(1) and Ru(2) is almost symmetrical [Ru(1)–C(7) 2.13(2), Ru(2)–C(7) 2.12(2) Å], whereas the C(10)–O(10) bridge



Scheme 1 Synthetic routes to clusters **1**–**4**

across Ru(1)–Ru(3) is semi-bridging [Ru(1)–C(10) 2.59(2), Ru(3)–C(10) 1.96(2) Å]. This is in line with the Ru(3)–C(10)–O(10) angle of 161.7(13)°. The carbonyl ligands bridging the Ru–Ir edges form dihedral angles of 3.2(4)° [for C(1)–O(1)] and 5.3(5)° [for C(4)–O(4)] with the Ir(1)–Ru(1)–Ru(2) plane and are nearly co-planar. The semi-bridging CO group across Ru(1)–Ru(3) is also almost co-planar with the ruthenium triangle [4.8(4)°]. By contrast, the CO-bridge across Ru(1)–Ru(2) lies out of the Ir(1)–Ru(1)–Ru(2) plane, the torsion angle being 10.2(4)°.

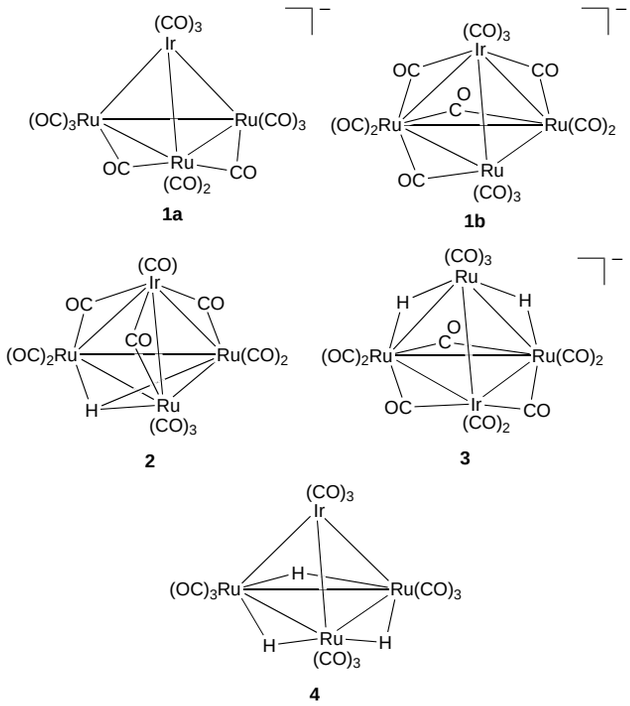
The intramolecular mobility of the carbonyl ligands in the cluster anion $[Ru_3Ir(CO)_{13}]^-$ **1** was studied by variable-temperature ^{13}C NMR spectroscopy. At room temperature only one sharp signal was observed at δ 199.4 (in $CDCl_3$) for the 13 CO groups in **1**, being indicative of a complete carbonyl scrambling about the Ru_3Ir metal core. At −60 °C the carbonyl resonance (δ 201.6) broadens, but even at −120 °C (in CD_2Cl_2–$CHCl_2F$) the broad signal at δ 200.4 is still present, while two extremely weak and broad additional signals appear at δ 193 and 176. This means that even at −120 °C the low-temperature limiting spectrum is not achieved.

These findings demonstrate the carbonyl envelope in $[Ru_3Ir(CO)_{13}]^-$ **1** to be extremely fluxional: in solution all 13 carbonyl ligands are equivalent on the NMR time-scale down to −60 °C. This is not surprising, since two isomers having a different carbonyl arrangement (**1a** and **1b**) are even found in the crystal of the $[N(PPh_3)_2]^+$ salt of **1**. This is in contrast to the findings for the neutral tetranuclear metal carbonyls $[Co_4(CO)_{12}]$,[11] $[Rh(CO)_4]$,[11,12] $[Ir_4(CO)_{12}]$,[11] $[Ir_2Rh_2(CO)_{12}]$[12] and $[RhCo_3(CO)_{12}]$[13] which have a more restricted pattern of carbonyl mobility.

Reactions of $[Ru_3Ir(CO)_{13}]^-$ with H^+ and H_2

The cluster anion $[Ru_3Ir(CO)_{13}]^-$ **1** reacts at ambient temperature with an excess of $HBF_4{\cdot}OEt_2$ in dichloromethane to give quantitatively the neutral red cluster $[HRu_3Ir(CO)_{13}]$ **2** (Scheme 1), which can be isolated by preparative thin-layer chromatography. It was not possible to protonate **1** {$[N(PPh_3)_2]^+$ salt} with H_3PO_4, this being in line with similar findings for the cobalt homologue.[6] Complex **2** is soluble in polar as well as in non-polar organic solvents.

The IR spectrum of **2** shows four absorptions in the region of terminal carbonyl ligands, a weak broad band at 1874 cm^{-1} identified as bridging CO groups. Only one singlet signal is found in the hydride region of the ^1H NMR spectrum at δ −17.93, which indicates that **2** is present only in the form of one isomer. The mass spectrum exhibits the parent ion peak at *m*/*z* 861 (M^+; ^{101}Ru, ^{193}Ir) followed by a series of fragments $[HRu_3Ir(CO)_n]^+$ (n = 1–12). All spectroscopic data suggest **2** to have the same ligand arrangement as proposed for the isoelectronic cluster $[HRu_3Co(CO)_{13}]$.[6] Accordingly, the tetrahedral



Scheme 2 Molecular constitution of the tetranuclear clusters **1** and **3** (found), as well as **2** and **4** (proposed)

Ru_3Ir core of **2** is supposed to possess three μ_2-carbonyl bridges and a μ_3-H cap over the triruthenium face (Scheme 2).

The reaction of $[Ru_3Ir(CO)_{13}]^-$ **1** with molecular hydrogen under refluxing conditions leads, with loss of one CO ligand, to the anionic dihydrido cluster $[H_2Ru_3Ir(CO)_{12}]^-$ **3** (Scheme 1), which is isoelectronic with the known cobalt and rhodium clusters $[H_2Ru_3Co(CO)_{12}]^-$ [14] and $[H_2Ru_3Rh(CO)_{12}]^-$.[15] Thus, the new cluster anion **3** is accessible in the same way as the known cobalt homologue, whereas the rhodium homologue has been prepared by a different method, starting from $[HRu_3(CO)_{11}]^-$ and $[Rh(CO)_4Cl_2]$.[15] Anion **3** can be isolated as the bis(triphenylphosphoranylidene)ammonium salt in good yields giving brown-yellow air-stable crystals, which are soluble in polar and non-polar organic solvents such as thf, diethyl ether, dichloromethane or methanol. The IR spectrum of **3** shows five vibrations for terminal carbonyl groups and two absorptions indicating bridging CO ligands (Table 1), the pattern being similar to that of the structurally characterized complex $[H_2Ru_3Rh(CO)_{12}]^-$.[15] The ^1H NMR spectrum of **3** shows a multiplet centred at δ 7.55 for the $[N(PPh_3)_2]^+$ cation and a sharp singlet at δ −20.64 corresponding to the two equivalent hydride ligands. The hydride resonance does not change over a temperature range of 20 to −55 °C.

The molecular structure of $[H_2Ru_3Ir(CO)_{12}]^-$ **3** comprises a tetrahedral arrangement of the four metal atoms. The crystal structure consists of discrete cations and anions with normal intermolecular contacts between the atoms of the ions. A ZORTEP[16] plot of **3** is shown in Fig. 3, selected bonds and angles are reported in Table 4.

The Ru_3Ir tetrahedron is distorted because of the two bridging hydride ligands. Whereas in the basic triangle Ir(1)–Ru(1)–Ru(3) the bond lengths are in the same range (between 2.74 and 2.78 Å), the distances of these three metal atoms to Ru(2) are all different. The Ru(1)–Ru(2) and Ru(2)–Ru(3) edges, bridged by a μ_2-hydride ligand, are longer [Ru(1)–Ru(2) 2.9530(9), Ru(2)–Ru(3) 2.9826(9) Å] than the non-bridged Ir(1)–Ru(2) edge [2.7799(7) Å]. These distances compare well with hydrido-bridged Ru–Ru bonds in other ruthenium or mixed-metal clusters.[10,15,17] A repulsion between the hydride ligands and the nearest equatorial CO groups is observed, the bond angles being 112.2(2)° for Ru(2)–Ru(1)–C(7) and

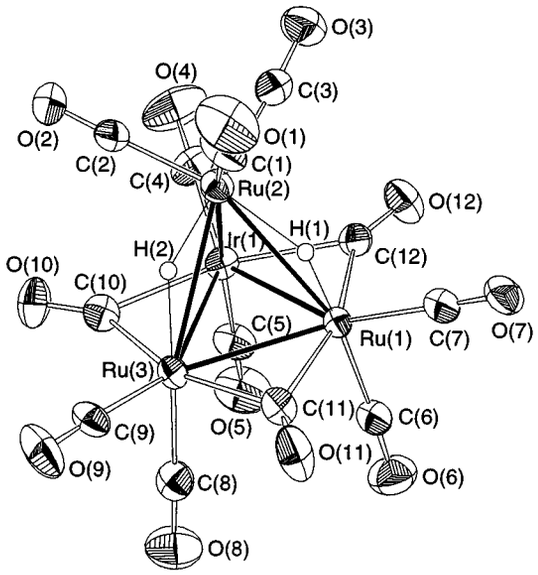


Fig. 3 Molecular structure of cluster anion **3**

Table 4 Selected bond lengths (Å) and angles (°) for anion **3**

Ru(1)–Ru(2)	2.9530(9)	Ru(2)–H(2)	1.61(8)
Ru(1)–Ru(3)	2.7804(8)	Ru(3)–H(2)	1.87(9)
Ru(2)–Ru(3)	2.9826(9)	Ru(1)–C(11)	2.127(7)
Ir(1)–Ru(1)	2.7412(8)	Ru(3)–C(11)	2.136(8)
Ir(1)–Ru(2)	2.7799(7)	Ru(3)–C(10)	2.066(7)
Ir(1)–Ru(3)	2.7466(7)	Ir(1)–C(10)	2.166(7)
Ru(1)–H(1)	1.50(8)	Ru(1)–C(12)	2.055(7)
Ru(2)–H(1)	1.76(8)	Ir(1)–C(12)	2.201(7)
Ru(1)–Ru(2)–Ru(3)	55.86(2)	Ru(2)–Ru(1)–H(1)	27(3)
Ru(1)–Ru(3)–Ru(2)	61.53(2)	Ru(2)–Ru(3)–H(2)	28(3)
Ru(3)–Ru(1)–Ru(2)	62.61(2)	Ru(3)–Ru(2)–H(2)	34(3)
Ru(1)–Ir(1)–Ru(2)	64.67(2)	Ru(1)–C(11)–O(11)	140.6(6)
Ru(1)–Ir(1)–Ru(3)	60.88(2)	Ru(3)–C(11)–O(11)	137.7(6)
Ru(3)–Ir(1)–Ru(2)	65.32(2)	Ru(1)–C(11)–Ru(3)	81.4(3)
Ir(1)–Ru(1)–Ru(2)	58.30(2)	Ru(3)–C(10)–O(10)	145.0(6)
Ir(1)–Ru(2)–Ru(1)	57.03(2)	Ir(1)–C(10)–O(11)	134.1(6)
Ir(1)–Ru(1)–Ru(3)	59.65(2)	Ru(3)–C(10)–Ir(1)	80.9(3)
Ir(1)–Ru(3)–Ru(1)	59.46(2)	Ru(1)–C(12)–O(12)	145.6(6)
Ir(1)–Ru(2)–Ru(3)	56.80(2)	Ir(1)–C(12)–O(12)	134.2(6)
Ir(1)–Ru(3)–Ru(2)	57.88(2)	Ru(1)–C(12)–Ir(1)	80.1(2)
Ru(1)–Ru(2)–H(1)	23(3)		

115.6(2)° for Ru(2)–Ru(3)–C(9), whereas the non-bridged edge forms an Ru(2)–Ir(1)–C(4) angle of only 99.0(2)°. The carbonyl ligand arrangement is similar to that of the isoelectronic $[H_2Ru_3Rh(CO)_{12}]^-$ anion.[15] In the Ir(1)–Ru(1)–Ru(3) triangle, each metal atom carries two terminal carbonyl ligands and is involved in two carbonyl bridges, each metal–metal bond being almost symmetrically bridged by a CO ligand. Atom Ru(2) carries only three terminal carbonyl groups. The three bridging carbonyls lie in the Ir(1)–Ru(1)–Ru(3) plane, the dihedral angles being 2.2(2), 0.8(2) and 0.4(2)°, respectively.

The hydrogenation of the neutral cluster $[HRu_3Ir(CO)_{13}]$ **2** under refluxing conditions in hexane solution affords the neutral trihydrido cluster $[H_3Ru_3Ir(CO)_{12}]$ **4**. The reaction is monitored by a colour change from red to yellow. The air-stable product **4** crystallizes directly from the reaction mixture as yellow crystals upon cooling. Cluster **4** is also accessible by protonation of anion **3** with $HBF_4{\cdot}OEt_2$ in dichloromethane. This reaction is reversible; treatment of **4** with K-Selectride {$KB[CH(Me)C_2H_5]_3H$, 1.0 M in thf} causes the reformation of **3**, as indicated by the IR spectrum. The neutral cluster $[H_3Ru_3Ir(CO)_{12}]$ **4** is soluble in thf and only slightly soluble in other organic solvents. In the IR spectrum of **4** four vibrations in the region of the terminal carbonyl ligands are observed, similar to $[H_3Ru_3Rh(CO)_{12}]$,[18] whereas the IR spectrum of the cobalt homologue $[H_3Ru_3Co(CO)_{12}]$ is more complex, due to the presence of two isomers in solution.[19] The ^1H NMR spectrum of **4** gives rise to only one sharp singlet signal at δ −17.93, which does not change over a temperature range from 20 to −55 °C. On the basis of spectroscopic data it is therefore assumed that **4** presents the same ligand arrangement as $[H_3Ru_3Rh(CO)_{12}]$.[18] Each of the four metal atoms of the Ru_3Ir tetrahedron carries three terminal carbonyl ligands, the three μ_2-hydrido ligands bridge the three metal–metal bonds of the Ru_3 triangular face (Scheme 2).

Experimental

All reactions were carried out in an atmosphere of nitrogen using standard Schlenk techniques. Solvents were distilled over drying agents and deoxygenated and nitrogen-saturated prior to use.[20] Preparative thin-layer chromatography was performed using 20 × 20 cm plates coated with FLUKA silica gel G. The compound $IrCl_3{\cdot}xH_2O$ (Strem) and $[N(PPh_3)_2]Cl$ (Fluka) were purchased and used as received. The compounds $[Ru_3(CO)_{12}]$,[21] $[Ir_4(CO)_{12}]$[22] and $[N(PPh_3)_2][Ir(CO)_4]$[23] were prepared according to literature methods. Nuclear magnetic resonance spectra were recorded using a Varian Gemini 200 BB instrument or a Bruker AMX 400 spectrometer and referenced by using the resonances of residual protons in the deuteriated solvents. Infrared spectra were recorded with a Perkin-Elmer 1720X FT-IR spectrometer. Mass spectra were measured by Professor T. A. Jenny, University of Fribourg, Switzerland. Microanalyses were carried out by the Mikroelementaranalytisches Laboratorium of the ETH Zürich, Switzerland.

Preparations

$[N(PPh_3)_2][Ru_3Ir(CO)_{13}]$ (anion 1). A solution of $[Ru_3(CO)_{12}]$ (115 mg, 0.18 mmol) and $[N(PPh_3)_2][Ir(CO)_4]$ (100 mg, 0.18 mmol) in thf (30 ml) was stirred under reflux for 1 h. After removal of the solvent the brown residue was dissolved in diethyl ether (10 ml) and filtered; addition of hexane (20 ml) under vigorous stirring caused the precipitation of $[N(PPh_3)_2][Ru_3Ir(CO)_{13}]$; it was isolated by decantation as a red-brown microcrystalline powder (210.2 mg, 84%) (Found: C, 42.07; H, 2.35; N, 0.92. $C_{49}H_{30}IrNO_{13}P_2Ru_3$ requires C, 42.09; H, 2.16; N, 1.00%).

$[HRu_3Ir(CO)_{13}]$ 2. To a stirred solution of **1** (75 mg, 0.054 mmol) in CH_2Cl_2 (30 ml) a slight excess of $HBF_4{\cdot}OEt_2$ (54%, 30 μl) was added. After 15 min the solvent was evaporated and the residue redissolved in the minimum quantity of CH_2Cl_2. The solution was separated by thin-layer chromatography using a mixture of CH_2Cl_2 and cyclohexane (2:3) as eluent. The red band containing **2** was extracted with CH_2Cl_2, followed by evaporation to dryness to give the product as a red powder (39.7 mg, 86%) (Found: C, 18.34; H, 0.19. $C_{13}HIrO_{13}Ru_3$ requires C, 18.14; H, 0.12%).

$[N(PPh_3)_2][H_2Ru_3Ir(CO)_{12}]$ (anion 3). *Method* (*a*). A solution containing complex **1** (100 mg, 0.071 mmol) in thf (30 ml) was placed in a pressure Schlenk tube and heated for 20 h to 80 °C under a pressure of 2 bar of hydrogen. After removing the solvent, the residue was dissolved in diethyl ether and filtered. Addition of an equal volume of hexane to the solution gave brown-yellow crystals of **3** (79.5 mg, 81%) (Found: C, 41.93; H, 2.17; N, 1.08. $C_{48}H_{32}IrNO_{12}P_2Ru_3$ requires C, 42.02; H, 2.35; N, 1.02%).

Method (*b*). The complex $[H_3Ru_3Ir(CO)_{12}]$ **4** (20 mg, 0.024 mmol) in thf (25 ml) was treated at room temperature with an excess of K-Selectride in thf solution (1 M, 40 μl) during 20 h. The complete formation of $[H_2Ru_3Ir(CO)_{12}]^-$ **3** was confirmed by IR spectroscopy.

Table 5 Crystallographic data for the $[N(PPh_3)_2]^+$ salts of **1** and **3**

	1	**3**
Formula	$C_{49}H_{30}IrNO_{13}P_2Ru_3$	$C_{48}H_{32}IrNO_{12}P_2Ru_3$
M	1398.15	1372.16
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	16.650(8)	14.726(2)
b/Å	19.793(9)	19.613(2)
c/Å	25.580(10)	16.931(4)
α/°	69.96(3)	—
β/°	70.83(5)	99.188(13)
γ/°	82.35(4)	—
U/Å^3	7478(6)	4827(2)
Z	6	4
Crystal dimensions/mm	0.42 × 0.23 × 0.19	0.46 × 0.27 × 0.23
Colour	Red	Brown
D_c/g cm^{-3}	1.863	1.888
μ/mm^{-1}	3.477	3.588
Transmission factors: min, max	0.831, 1.214	0.719, 1.335
F(000)	4044	2648
θ limits/°	2.08–20.00	2.08–25.51
hkl Ranges	−15 to 16, −17 to 19, 0–24	−17 to 17, 0–23, 0–20
Reflections measured	13916	8987
Independent reflections	13916	8987
Observed reflections	11261	7519
$R1[I > 2\sigma(I)]$, $R1$ (all data)[a]	0.0490, 0.0709	0.0454, 0.0831
$wR2[I > 2\sigma(I)]$, $wR2$ (all data)[b]	0.0920, 0.1017	0.0632, 0.1127
Goodness of fit on F^2[c]	1.073	1.115

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^4]^{\frac{1}{2}}$. [c] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{\frac{1}{2}}$ (n = number of reflections, p = number of parameters).

$[H_3Ru_3Ir(CO)_{12}]$ 4. The complex $[HRu_3Ir(CO)_{13}]$ **2** (50 mg, 0.06 mmol) was dissolved in hexane (30 ml) and placed in a pressure Schlenk tube under a pressure of 2 bar of hydrogen. The solution was heated to 80 °C for 30 min, during which time the colour changed from red to yellow. By cooling the solution to room temperature, yellow crystals of **4** formed and were filtered off. A second crop of product was collected after evaporation of the residual solution under reduced pressure (44.6 mg, 92%) (Found: C, 17.47; H, 0.39. $C_{12}H_3IrO_{12}Ru_3$ requires C, 17.27; H, 0.36%).

Crystallography

Single crystals were obtained by slow diffusion of hexane into diethyl ether solution: red plates for the $[N(PPh_3)_2]^+$ salt of **1**, brown-yellow blocks for the $[N(PPh_3)_2]^+$ salt of **3**. The crystals of **1** {$[N(PPh_3)_2]^+$ salt} are slightly sensitive towards X-rays and decompose after prolonged irradiation. Selected crystallographic data for the two complexes are summarized in Table 5.

Data collection, solution and structure refinement. Single-crystal X-ray diffraction data were collected at −50 °C on a Stoe-Siemens AED2 four-circle diffractometer using Mo-Kα graphite-monochromated radiation (λ = 0.71073 Å; ω–2θ scans). The structures were solved by direct methods using the program SHELXS 86.[24] The structure refinement, using weighted full-matrix least squares on F^2, was carried out using the program SHELXL 93.[25] For the two compounds an empirical absorption correction was applied using DIFABS.[26] In the $[N(PPh_3)_2]^+$ salts of **1** and **3** the hydrogen atoms were included in calculated positions and refined as riding atoms using the SHELXL 93 default parameters. The hydride atoms in anion **3** were clearly localized from difference maps and refined isotropically. All non-hydrogen atoms in the $[N(PPh_3)_2]^+$ salts of **1** and **3** were refined anisotropically, except C(32) in the $[N(PPh_3)_2]^+$ cation of **1**, whose temperature factor was non-positive definite. The Figs. were drawn with ZORTEP[16] (thermal ellipsoids, 50% probability level).

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References

1 D. A. Roberts and G. L. Geoffroy, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, p. 763; R. D. Adams, in *Comprehensive Organometallic Chemistry 2*, eds. E. W. Abel, F. G. A. Stone and G. Wilkinson, Elsevier, Oxford, 1995, vol. 10, p. 1.
2 P. Braunstein and J. Rose, in *Comprehensive Organometallic Chemistry 2*, eds. E. W. Abel, F. G. A. Stone and G. Wilkinson, Elsevier, Oxford, 1995, vol. 10, p. 351.
3 G. Süss-Fink and G. Meister, *Adv. Organomet. Chem.*, 1993, **35**, 41.
4 G. Süss-Fink and F. Neumann, in *The Chemistry of the Metal-Carbon Bond*, ed. F. R. Hartley, Wiley, Chichester, 1989, vol. 5, p. 231.
5 C. S. Garland, M. F. Giles and J. G. Sunley, *Eur. Pat. App.* (to BP), 94306506.0, 1995.
6 P. C. Steinhardt, W. L. Gladfelter, A. D. Harley, J. R. Fox and G. L. Geoffroy, *Inorg. Chem.*, 1980, **19**, 332.
7 E. W. Burkhardt and G. L. Geoffroy, *J. Organomet. Chem.*, 1980, **198**, 179.
8 A. Fumagelli, D. Italia, M. C. Malatesta, G. Ciani, M. Moret and A. Sironi, *Inorg. Chem.*, 1996, **35**, 1765.
9 A. U. Härkönen, M. Ahlgrén, T. A. Pakkanen and J. Pursiainen, *J. Organomet. Chem.*, 1996, **519**, 205.
10 A. U. Härkönen, M. Ahlgrén, T. Pakkanen and J. Pursiainen, *Organometallics*, 1997, **16**, 689.
11 B. F. G. Johnson and R. E. Benfield, *J. Chem. Soc.*, *Dalton Trans.*, 1978, 1554.
12 R. Roulet, *Chimia*, 1996, **50**, 629.
13 B. F. G. Johnson, J. Lewis and T. W. Matheson, *J. Chem. Soc.*, *Chem. Commum.*, 1974, 441.
14 D. E. Fjare, D. G. Keyes and W. L. Gladfelter, *J. Organomet. Chem.*, 1983, **250**, 383.
15 H. J. Kakkonen, M. Ahlgrén, T. A. Pakkanen and J. Pursiainen, *J. Organomet. Chem.*, 1994, **482**, 279.
16 C. K. Johnson, ZORTEP, Oak Ridge National Laboratory, Oak Ridge, TN, modified for PC by L. Zsolnai and H. Pritzkow, University of Heidelberg, 1994.
17 D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, 1972, **4**, 838.
18 J. Pursiainen and T. A. Pakkanen, *J. Chem. Soc.*, *Dalton Trans.*, 1989, 2449.
19 W. L. Gladfelter, G. L. Geoffroy and J. C. Calabrese, *Inorg. Chem.*, 1980, **19**, 2569.
20 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 3rd edn., 1988.
21 M. I. Bruce, C. M. Jensen and N. L. Jones, *Inorg. Synth.*, 1989, **26**, 259.
22 R. D. Pergola, L. Garlaschelli and S. Martinengo, *Inorg. Synth.*, 1990, **28**, 245.
23 L. Garlaschelli, P.Chini and S. Martinengo, *Gazz. Chim. Ital.*, 1982, **112**, 285.
24 G. M. Sheldrick, *Acta Crystallogr.*, *Sect.A*, 1990, **46**, 467.
25 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.
26 N. Walker and D. Stuart, *Acta Crystallogr.*, *Sect.A*, 1990, **46,** 158.

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