

Synthesis and Characterization of Pentanuclear Fe–Ir Carbonyl Clusters. Solid-state Structures of $[\text{N}(\text{PPh}_3)_2]_2[\text{FeIr}_4(\text{CO})_{15}]$ and $[\text{PPh}_4][\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]^\dagger$

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The dianion $[\text{FeIr}_4(\text{CO})_{15}]^{2-}$ can be obtained by reduction of an equimolar mixture of $[\text{Fe}(\text{CO})_5]$ and $[\text{Ir}_4(\text{CO})_{12}]$ in alcoholic NaOH and under 1 atm of carbon monoxide. The salt $[\text{N}(\text{PPh}_3)_2]_2[\text{FeIr}_4(\text{CO})_{15}]$ (**1**) crystallizes in the triclinic space group $P\bar{1}$ with unit-cell dimensions $a = 11.399(3)$, $b = 14.032(3)$, $c = 29.163(4)$ Å, $\alpha = 86.18(2)$, $\beta = 84.52(2)$, $\gamma = 80.14(2)^\circ$, and $Z = 2$. Its metal framework consists of a trigonal bipyramid with the equatorial triangle formed by iridium atoms. The mean values of the Fe–Ir, $\text{Ir}_{\text{eq}}\text{--}\text{Ir}_{\text{eq}}$, and $\text{Ir}_{\text{ap}}\text{--}\text{Ir}_{\text{eq}}$ distances are 2.943, 2.708, 2.991 Å, respectively. The monoanion $[\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]^-$ was obtained from $[\text{Fe}(\text{CO})_4]^{2-}$ and $[\text{Ir}(\text{CO})_2\text{Cl}_2]^-$. The salt $[\text{PPh}_4][\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]$ (**2**) crystallizes in the orthorhombic space group $P2_12_12_1$ with unit-cell dimensions $a = 12.461(5)$, $b = 14.306(5)$, $c = 23.504(6)$ Å, and $Z = 4$. Its metallic framework is comprised of an iridium triangle capped on opposite sides by two iron atoms. The mean values of the Fe–Ir and Ir–Ir distances are 2.648 and 2.708 Å, respectively. In the derivative (**1**) the trigonal bipyramid is considerably elongated in the direction of the apical atoms, when compared with that in (**2**). This elongation is consistent with the increased number of cluster valence electrons: 76 in (**1**) and 72 in (**2**).

Transition-metal clusters are attracting a great deal of interest with respect to their potential as catalysts. Particularly mixed-metal clusters are extensively studied because adjacent metal centres formed by different elements offer the possibility for co-operative reactions leading to new, more active, or more selective catalysts.^{1–3} Moreover, they should act as potential precursors of bimetallic heterogeneous catalysts of well defined stoichiometry.⁴

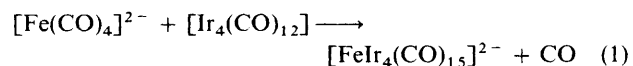
The lack of an extensive work on Fe–Ir bimetallic clusters⁵ and recent reports on Fe–Ir traditional catalysts, very selective for the production of MeOH from CO and H₂,^{6–8} prompted us to investigate this field. In this paper we describe the synthesis, the chemical characterization, and the solid-state structures of the two new clusters $[\text{N}(\text{PPh}_3)_2]_2[\text{FeIr}_4(\text{CO})_{15}]$ (**1**) and $[\text{PPh}_4][\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]$ (**2**), the first examples of Fe–Ir mixed-metal carbonyl clusters.

Results and Discussion

Preparation of $[\text{FeIr}_4(\text{CO})_{15}]^{2-}$ (1**).—**The extensive work done on mixed-metal pentanuclear carbonyl clusters of Group 8 metals^{9–15} suggested that the dianion $[\text{FeIr}_4(\text{CO})_{15}]^{2-}$ (**1**) should be investigated first, in order to compare its structure and chemical behaviour with those of the already reported and strictly related derivatives $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$ (**3**),⁹ $[\text{RuRh}_4$

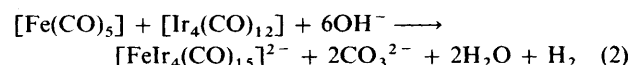
$(\text{CO})_{15}]^{2-}$ (**4**),¹⁰ and $[\text{RuIr}_4(\text{CO})_{15}]^{2-}$ (**5**).¹⁴ Two synthetic procedures were devised for the preparation of (**1**), *i.e.* (i) the redox condensation of $[\text{Fe}(\text{CO})_4]^{2-}$ on the neutral carbonyl $[\text{Ir}_4(\text{CO})_{12}]$, since this type of reaction had previously been used for the preparation of (**3**) in almost quantitative yields, and (ii) the reduction–condensation of the neutral carbonyls $[\text{Fe}(\text{CO})_5]$ and $[\text{Ir}_4(\text{CO})_{12}]$ under 1 atm of carbon monoxide in a methanolic solution of NaOH, as employed for the synthesis of (**5**). Only the latter method proved to be successful, and anion (**1**) could be isolated in good yields.

According to the first synthetic procedure, the reaction of $\text{Na}_2[\text{Fe}(\text{CO})_4]$ with $[\text{Ir}_4(\text{CO})_{12}]$, in a molar ratio 1:1, which displays the right ratio between the number of metal atoms and the negative charges, can be represented by equation (1). The



reaction was performed in anhydrous tetrahydrofuran (thf), under 1 atm of carbon monoxide. However, only very low yields (about 5%) of the expected compound could be obtained, since the two monoanions $[\text{FeH}(\text{CO})_4]^-$ and $[\text{Ir}_4\text{H}(\text{CO})_{11}]^-$ are immediately formed, and these two species are not reactive under the experimental conditions. The hydrido carbonyl compounds are probably produced *via* radical anions and subsequent hydrogen abstraction from the solvent.

The second method starts from a mixture of $[\text{Fe}(\text{CO})_5]$ and $[\text{Ir}_4(\text{CO})_{12}]$, in a molar ratio of 1:1, this stoichiometry being based on the metal ratio in the final product (**1**). Best results are obtained with a slight excess of $[\text{Fe}(\text{CO})_5]$ in methanolic NaOH, under 1 atm of CO, according to equation (2). *I.r.*



† Bis[bis(triphenylphosphine)iminium] 1,2,2,3,2,4;3,4,3,5,4,5-hexa- μ -carbonyl-1,1,1,2,3,4,5,5,5-nonacarbonyl-*cyclo*-1,2,3,4-tetra-iridium-5-ferrate (6Ir–Ir, 3Ir–Fe) and tetraphenylphosphonium 1,2,1,3,3,5,4,5-tetra- μ -carbonyl-1,1,2,2,3,3,4,4,4,5,5-decacarbonyl-2,3,4-tri-iridium-1,5-diferrate (3Ir–Ir, 6Ir–Fe).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii–xx.

Non-S.I. unit employed: atm = 101 325 Pa.

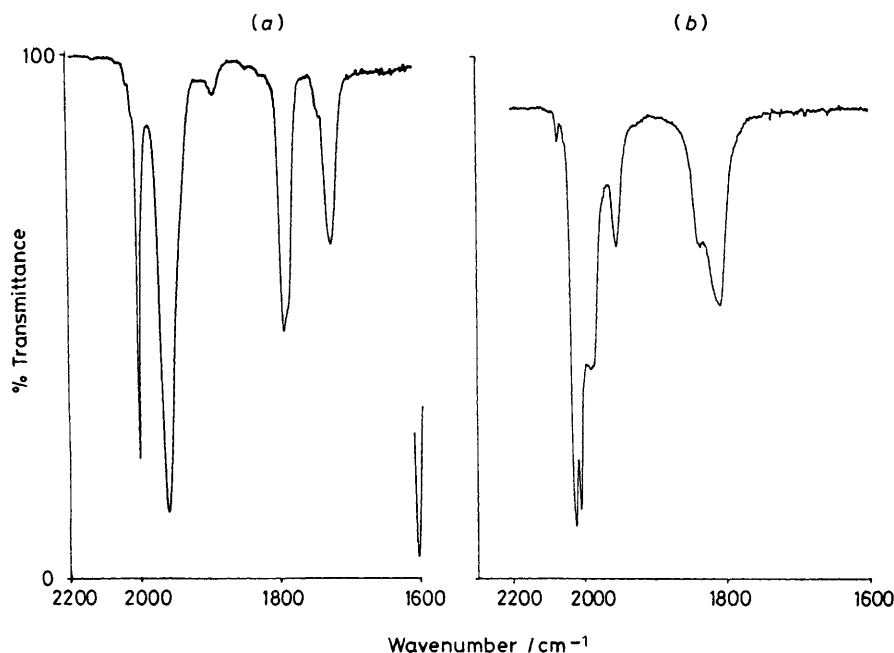
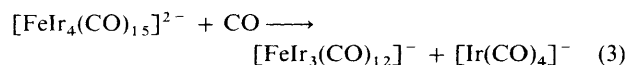


Figure 1. (a) Infrared spectrum of $[\text{N}(\text{PPh}_3)_2]_2[\text{FeIr}_4(\text{CO})_{15}]$ in thf. The $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$ salt (thf solution) shows bands at 2011s, 1965vs, 1794ms, 1780m, 1717mw, and 1698mw cm^{-1} , (MeCN solution) at 2014s, 1966vs, 1784ms, and 1717m cm^{-1} . (b) I.r. spectrum of $[\text{PPh}_4]^+[\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]^-$ in thf

monitoring of the solution shows that, in the first step, the two carbonyls are transformed into $[\text{Ir}_4\text{H}(\text{CO})_{11}]^-$ ¹⁶ and $[\text{FeH}(\text{CO})_4]^-$ ¹⁷ and in the presence of concentrated NaOH they condense to produce (1) with hydrogen evolution, which was clearly detected by gas chromatography in the reaction vessel. In reaction (2) carbon monoxide is not required as a reagent but is necessary in order to stabilize the product, which is only moderately stable under a nitrogen atmosphere. The use of mononuclear $[\text{Fe}(\text{CO})_5]$, instead of $[\text{Fe}_3(\text{CO})_{12}]$, as starting material significantly increases the yield of (1) when compared with the yields reported for $[\text{N}(\text{PPh}_3)_2]_2[\text{RuIr}_4(\text{CO})_{15}]$: in the latter case an eight-fold excess of Ru atoms was necessary, and less than 20% of product could be obtained.¹⁴

The dianion can be recovered, after about 6 h, by addition of a bulky cation to the reaction slurry. The $[\text{N}(\text{PPh}_3)_2]^+$ cation is by far the most suitable for the isolation of $[\text{FeIr}_4(\text{CO})_{15}]^{2-}$, since, with smaller tetrasubstituted ammonium cations such as $[\text{NEt}_4]^+$ or $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$, the isolation of the pure product is much more difficult and, sometimes, decomposition occurs, whereas tetrasubstituted phosphonium salts are not stable in such a strong alkaline medium.¹⁸ The $[\text{N}(\text{PPh}_3)_2]^+$ salt of (1) can be crystallized from thf-cyclohexane or -2-propanol.

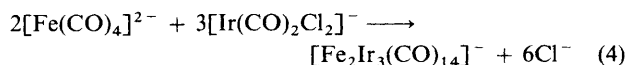
The i.r. spectrum of $[\text{N}(\text{PPh}_3)_2]_2[\text{FeIr}_4(\text{CO})_{15}]$ in thf solution, represented in Figure 1(a), shows bands at 2003s, 1959vs, 1791ms, and 1725m cm^{-1} , with a pattern very similar to that of the dianions (3)–(5) which exhibit the same structure.^{9,10,14} Compound (1) must be handled and kept under 1 atm of carbon monoxide, although, on prolonged standing in solution, an appreciable fragmentation was observed, with the formation of $[\text{Ir}(\text{CO})_4]^-$ and a yellow derivative. Thus, when solutions of (1) are layered with a precipitating agent, in order to obtain crystalline samples, some crystals of $[\text{N}(\text{PPh}_3)_2][\text{Ir}(\text{CO})_4]^-$ are formed, and the yellow cluster is left in the mother-liquor. A possible formulation for the yellow product obtained from the fragmentation [equation (3)] of (1) is



$[\text{N}(\text{PPh}_3)_2][\text{FeIr}_3(\text{CO})_{12}]$. The i.r. spectrum, in thf solution, of the tetranuclear anion, $\nu(\text{CO})$ 2033vs, 1997vs, 1979 (sh), 1940w, 1824m, and 1809m cm^{-1} , is reminiscent of that of other tetranuclear compounds of iridium such as $[\text{Ir}_4(\text{CO})_{11}\text{Br}]^-$.¹⁹

When complex (1) is dissolved in thf under nitrogen, a more rapid, but much less selective, decomposition is observed, which yields small amounts of $[\text{Ir}(\text{CO})_4]^-$ and $[\text{FeIr}_3(\text{CO})_{12}]^-$ and a brown product sparingly soluble in thf, whose i.r. spectrum shows bands at 1975vs, 1955s, 1935m, 1780m, and 1750m cm^{-1} . This product could not be characterized since the crystals obtained had a very poor diffracting power. However, it seems likely that it is a new bimetallic derivative because its i.r. spectrum cannot be assigned to any known homometallic cluster of either iridium or iron. This reactivity resembles the behaviour of $[\text{RuIr}_4(\text{CO})_{15}]^{2-}$,¹⁴ which in the absence of carbon monoxide produces an uncharacterized brown product together with the tetranuclear derivative $[\text{RuIr}_3(\text{CO})_{12}]^-$.²⁰ This similarity further supports the formulation of the yellow compound as $[\text{FeIr}_3(\text{CO})_{12}]^-$.

Preparation of $[\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]^-$ (2).—The reaction of the strong nucleophile $[\text{Fe}(\text{CO})_4]^{2-}$ with several carbonyl derivatives of iridium has been investigated. The complex $[\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]^-$ (2) can be obtained in about 40% yield from $[\text{Fe}(\text{CO})_4]^{2-}$ and $[\text{Ir}(\text{CO})_2\text{Cl}_2]^-$, in a molar ratio of 2:3. The overall reaction can be represented by equation (4). This



reaction, carried out in thf, is very rapid at the beginning and slows down after a few minutes; however it is not selective, and a rather complex mixture of compounds is obtained even after a longer period of time. Thus, the i.r. spectrum of the solution shows the presence of a large number of carbonylic compounds, which do not re-equilibrate to give a unique product. However, all these compounds are forced to condense together and afford slightly impure $[\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]^-$ in the following step, when the solvent is removed *in vacuo* and the crude residue is

Table 1. Selected distances (Å) and angles (°) in the dianion $[\text{FeIr}_4(\text{CO})_{15}]^{2-}$ (1) with estimated standard deviations (e.s.d.s) on the last figure in parentheses

Metal-metal		Metal-C _(bridging) -metal	
Ir(1)-Ir(2)	2.727(1)	Ir(1)-CD(12)-Ir(2)	85(1)
Ir(1)-Ir(3)	2.719(1)	Ir(1)-CD(13)-Ir(3)	83(1)
Ir(1)-Ir(4)	2.968(1)	Ir(1)-CD(14)-Ir(4)	98(1)
Ir(1)-Fe	2.927(3)	Ir(2)-CD(23)-Ir(3)	82(1)
Ir(2)-Ir(3)	2.678(1)	Ir(2)-CD(2)-Fe	96(1)
Ir(2)-Ir(4)	3.000(1)	Ir(3)-CD(3)-Fe	93(1)
Ir(2)-Fe	2.949(3)		
Ir(3)-Ir(4)	3.004(1)	Metal-C-O _(bridging)	
Ir(3)-Fe	2.953(3)	Ir(1)-CD(12)-OD(12)	139(2)
		Ir(1)-CD(13)-OD(13)	140(2)
Metal-carbon _{terminal} *		Ir(1)-CD(14)-OD(14)	127(2)
Ir-C	1.79	Ir(2)-CD(12)-OD(12)	135(2)
Fe-C	1.72	Ir(2)-CD(23)-OD(23)	138(2)
		Ir(2)-CD(2)-OD(2)	131(2)
Metal-carbon _{bridging} *		Ir(3)-CD(13)-OD(13)	137(2)
Ir-C	2.01	Ir(3)-CD(23)-OD(23)	137(2)
Fe-C	2.01	Ir(3)-CD(3)-OD(3)	133(2)
		Ir(4)-CD(14)-OD(14)	135(2)
C-O _{terminal} *		Fe-CD(2)-OD(2)	133(2)
Fe _{bonded}	1.17	Fe-CD(3)-OD(3)	134(2)
Ir _{bonded}	1.19		
C-O _{bridging} *	1.22		

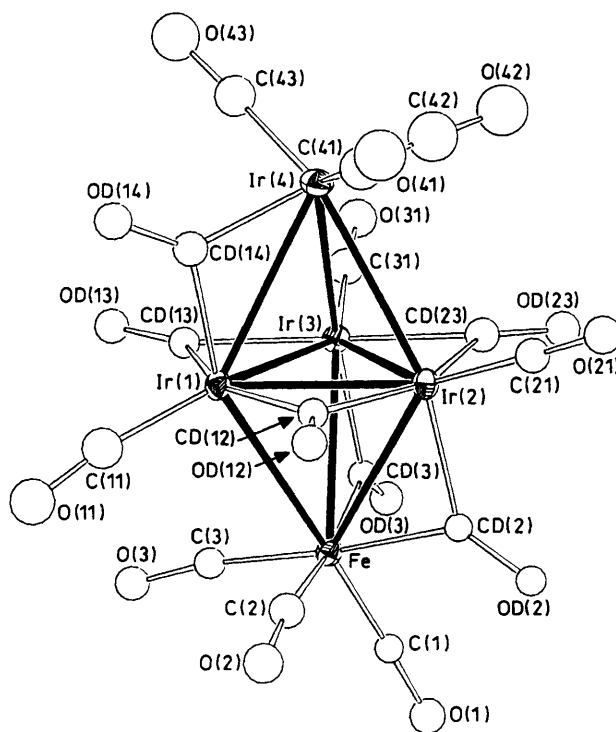
* Average value.

suspended in methanol. The phosphonium salt of this anion is well soluble and can be separated by filtration. From the methanolic solution, this cluster can be precipitated by addition of $[\text{PPh}_4]\text{Br}$ and water, and recrystallized from CH_2Cl_2 -cyclohexane or thf-cyclohexane. The i.r. spectrum of $[\text{PPh}_4][\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]$ shows bands [Figure 1(b)], in the CO stretching region, at 2 069vw, 2 020vs, 2 005s, 1 990 (sh), 1 952m, 1 834m, and 1 807ms cm^{-1} (thf), with intensities for terminal and bridging carbonyl groups consistent with a ratio of 5:2, found in the solid-state structure. The monoanion (2) is stable at room temperature under 1 atm of CO, since no traces of decomposition were observed after 24 h.

The same reaction at different Fe:Ir ratios and under different experimental conditions is currently under investigation. Preliminary results show that the bimetallic cluster which seems to be formed more frequently is a tetranuclear compound, presently formulated as $[\text{Fe}_2\text{Ir}_2(\text{CO})_{12}]^{2-}$, on the basis of elemental analysis and comparison of its i.r. spectrum with those of other tetranuclear anionic carbonyl clusters.

Crystal Structure of $[\text{N}(\text{PPh}_3)_2]_2[\text{FeIr}_4(\text{CO})_{15}]$ (1).—The solid-state structure of $[\text{N}(\text{PPh}_3)_2]_2[\text{FeIr}_4(\text{CO})_{15}]$, determined by X-ray single-crystal diffraction techniques, consists of a packing of discrete cations, anions, and clathrate thf molecules in the molar ratio 2:1:2 with normal van der Waals contacts. A molecular plot of the dianion $[\text{FeIr}_4(\mu\text{-CO})_6(\text{CO})_9]^{2-}$ is presented in Figure 2, together with the atom labelling scheme; bond distances and angles are listed in Table 1.

The cluster consists of a trigonal bipyramid of metal atoms, with the iron atom located in one of the two apical positions. The cluster possesses approximate C_s point symmetry with a mirror plane passing through Fe, Ir(4), and Ir(1) and bisecting the Ir(2)-Ir(3) bond. Three terminal carbonyl groups are bonded to the apical atoms, whereas the three equatorial iridium atoms carry only one terminal carbonyl group each. Each equatorial metal is also bound to three bridging carbonyls:

**Figure 2.** ORTEP drawing of $[\text{FeIr}_4(\text{CO})_{15}]^{2-}$

two in the equatorial plane and one spanning the $\text{Ir}_{\text{eq}}\text{-M}_{\text{ap}}$ bond, in such a way that the iron atom possesses two $\mu\text{-CO}$ ligands and the Ir_{ap} only one. The carbonyl stereochemistry in compound (1) is the same as that previously found in $[\text{RuM}_4(\text{CO})_{15}]^{2-}$ ($\text{M} = \text{Rh}^{10}$ or Ir^{14}) and in $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$.

Mean metal-carbon distances for terminal CO groups are Ir(1-3)-C 1.76, Ir(4)-C 1.82, and Fe-C 1.72 Å, while the corresponding mean C-O distances are 1.20, 1.18, and 1.17 Å, respectively. The terminal carbon monoxide ligands are almost linear with an average M-C-O angle of 174° . Mean metal-carbon distances for bridging CO groups are Ir(1-3)-C 2.03 and Fe-C 2.01 Å, while the corresponding mean C-O distances are 1.23 and 1.19 Å, respectively.

The metal-metal interactions are in the range 2.678–3.004 Å but can be divided into three homogeneous groups: $\text{Ir}_{\text{eq}}\text{-Ir}_{\text{eq}}$ (mean 2.708), $\text{Ir}_{\text{eq}}\text{-Ir}_{\text{ap}}$ (mean 2.991), and $\text{Ir}_{\text{eq}}\text{-Fe}_{\text{ap}}$ (mean 2.943 Å). Thus, the distances observed in the central triangle are in the usual range found in other iridium dianions {see for example $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ 2.777 Å};²¹ whereas the $\text{Ir}_{\text{eq}}\text{-M}_{\text{ap}}$ are rather elongated and are in agreement with the corresponding distances found in $[\text{RuM}_4(\text{CO})_{15}]^{2-}$ ($\text{M} = \text{Rh}^{10}$ or Ir^{14}). These distances are scarcely affected by the presence of $\mu\text{-CO}$ groups; thus the bridged Fe- Ir_{eq} distances (av. 2.951 Å) are slightly longer than the unbridged Fe-Ir(1) [2.927(3) Å] whereas the bridged Ir(1)-Ir(4) [2.968(1) Å] is slightly shorter than the corresponding unbridged bond (av. 3.002 Å).

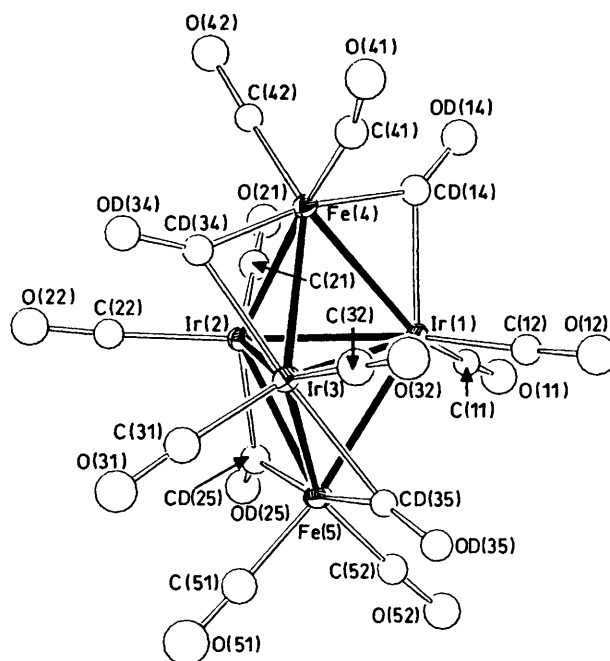
Crystal Structure of $[\text{PPh}_4][\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]$ (2).—The crystal structure of complex (2) consists of $[\text{PPh}_4]^+$ cations and $[\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]^-$ anions with normal van der Waals contact distances between the cations and the anions. An ORTEP view of $[\text{Fe}_2\text{Ir}_3(\mu\text{-CO})_4(\text{CO})_{10}]^-$ is presented in Figure 3 together with the atom labelling scheme. Selected bond distances and angles are listed in Table 2.

The metal framework of (2) is an idealized D_{3h} trigonal

Table 2. Selected distances (Å) and angles (°) in the anion $[\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]^-$ (2) with (e.s.d.s) on the last figure in parentheses

Metal-metal		Metal-C _{bridging} -metal	
Ir(1)-Ir(2)	2.664(1)	Ir(1)-CD(14)-Fe(4)	81(1)
Ir(1)-Ir(3)	2.718(1)	Ir(2)-CD(25)-Fe(5)	82(1)
Ir(1)-Fe(4)	2.622(2)	Ir(3)-CD(34)-Fe(4)	80(1)
Ir(1)-Fe(5)	2.710(3)	Ir(3)-CD(35)-Fe(5)	79(1)
Ir(2)-Ir(3)	2.741(1)		
Ir(2)-Fe(4)	2.695(2)	Metal-C _{bridging} -O	
Ir(2)-Fe(5)	2.606(3)	Ir(1)-CD(14)-OD(14)	134(2)
Ir(3)-Fe(4)	2.623(3)	Ir(2)-CD(25)-OD(25)	139(2)
Ir(3)-Fe(5)	2.623(3)	Ir(3)-CD(34)-OD(34)	130(2)
		Ir(3)-CD(35)-OD(35)	130(1)
Metal-carbon _{terminal} *		Fe(4)-CD(14)-OD(14)	144(2)
Ir-C	1.84	Fe(4)-CD(34)-OD(34)	149(2)
Fe-C	1.73	Fe(5)-CD(25)-OD(25)	139(2)
		Fe(5)-CD(35)-OD(35)	150(2)
Metal-carbon _{bridging} *			
Ir-C	2.14		
Fe-C	1.90		
C-O _{terminal} *			
Ir _{bonded}	1.16		
Fe _{bonded}	1.15		
C-O _{bridging}	1.18		

* Average value.

**Figure 3.** ORTEP drawing of $[\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]^-$

bipyramid, with a central triangle of iridium atoms and two capping iron atoms. The carbonyl ligands decrease the symmetry of the whole anion to C_2 , with the two-fold axis passing through Ir(3) and the midpoint of the Ir(1)-Ir(2) bond. Two terminal carbon monoxide groups are bonded to each metal atom, and the remaining CO groups are bridging four of the six Fe-Ir edges. Thus, the equatorial Ir(3) atom is connected to two bridging groups, Ir(1) and Ir(2) to one only: therefore, in the equatorial triangle, the system of three mutually adjacent bridging carbonyl groups, which appears almost constant in trigonal bipyramidal carbonyl clusters,^{10-12,14} is not present. Two bridging carbonyls, CD(14) and CD(25), can be considered symmetric, whereas the two μ -CO ligands bonded to Ir(3), CD(34) and CD(35), are clearly asymmetric, with the shorter length being toward the Fe (mean Ir-C 2.225, Fe-C 1.865 Å).

The metal-metal distances can be divided in three sets: Ir-Ir (mean 2.708), bridged Ir-Fe (mean 2.618), and unbridged Ir-Fe (2.702 Å). Therefore, in this monoanion, the bridging CO ligands significantly shorten the corresponding M-M bonds.

The polyhedra formed by the oxygen atoms of the ligands in complexes (1) and (2) are shown in Figure 4(a) and 4(b), respectively. The polyhedron observed in (2) can be described as based upon an hexagonal antiprism biccapped on the two opposite hexagonal faces; this arrangement, according to Johnson and Benfield,²² is the best way to pack fourteen ligands. For (1) a ligand polyhedron resembling the fourth favourable arrangement for fifteen CO groups can be recognized.

Conclusions

Several pentanuclear homometallic and bimetallic carbonyl clusters, with a bipyramidal metal arrangement and containing 72 or 76 cluster valence electrons (c.v.e.s), have been structurally characterized, such as $[\text{M}_2\text{Ni}_3(\text{CO})_{16}]^{2-}$ (M = Cr, Mo, or W),²³ $[\text{Os}_5(\text{CO})_{16}]$,²⁴ $[\text{Os}_5\text{H}(\text{CO})_{15}]^-$,²⁵ $[\text{Ni}_5(\text{CO})_{12}]^{2-}$,²⁶ $[\text{MRh}_4(\text{CO})_{15}]^{2-}$ (M = Fe⁹ or Ru¹⁰), $[\text{MRh}_4(\text{CO})_{15}]^-$ (M = Rh,²⁷ Co,²⁸ or Ir¹²), $[\text{PtM}_4(\text{CO})_{14}]^{2-}$ (M = Rh¹³ or Ir¹⁵),

$[\text{PtM}_4(\text{CO})_{12}]^{2-}$ (M = Rh¹³ or Ir¹⁵), $[\text{RuIr}_4(\text{CO})_{15}]^-$,¹⁴ and the recently reported $[\text{Ru}_5(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_4]$.²⁹ The species with 72 c.v.e.s are numerous when we consider both carbonyl and naked clusters of the post-transition metals,³⁰ but purely metal carbonyl compounds more frequently possess 76 c.v.e.s,³¹ and the poor-electron species can be related to the presence of Pt,¹³ Rh,¹³ or Ir¹⁵ atoms which preferably adopt a 16-electron configuration and square-planar co-ordination. On the contrary, (2) is an unusual example where the apical position is occupied by a metal which cannot assume this electronic configuration.

Anions (1) and (2) represent the first examples of Ir-Fe mixed-metal clusters. The chemistry of this bimetallic system appears to be promising and, up to now, several compounds have been detected. Unfortunately, the research in this field is not supported by the analogy with the already studied Fe-Rh system,⁹ since large differences, rather than similarities, are observed both in the synthesis and in the reactivity of the compounds.

Experimental

All reactions were carried out in an atmosphere of nitrogen or carbon monoxide with Schlenk-tube and vacuum-line techniques.³² Solvents were purified and dried by distillation under a nitrogen atmosphere from the following solvent-drier combinations: thf-sodium diphenylketyl, methanol-Mg, $\text{CH}_2\text{Cl}_2\text{-P}_2\text{O}_5$, and $\text{Pr}^i\text{OH-Al}(\text{OPr}^i)_3$. Infrared spectra were recorded on a Perkin-Elmer 781 spectrophotometer using calcium fluoride cells previously purged with nitrogen. The complexes $[\text{Ir}_4(\text{CO})_{12}]$,³³ $[\text{PPh}_4][\text{Ir}(\text{CO})_2\text{Cl}_2]$,³⁴ and $\text{Na}_2\text{-}[\text{Fe}(\text{CO})_4]$ ³⁵ were prepared as described previously.

Preparation of $[\text{N}(\text{PPh}_3)_2]_2[\text{FeIr}_4(\text{CO})_{15}]$ (1).—The complex $[\text{Ir}_4(\text{CO})_{12}]$ (1.104 g, 1.00 mmol) in a Schlenk tube was suspended in MeOH (20 cm³); the vessel was evacuated, carbon monoxide was admitted through a mercury valve, and vigorously stirred. Within a few minutes, required to saturate the solution of CO, NaOH (1.50 g, 37.5 mmol) was added and the mixture stirred until the $[\text{Ir}_4(\text{CO})_{12}]$ dissolved. At this stage

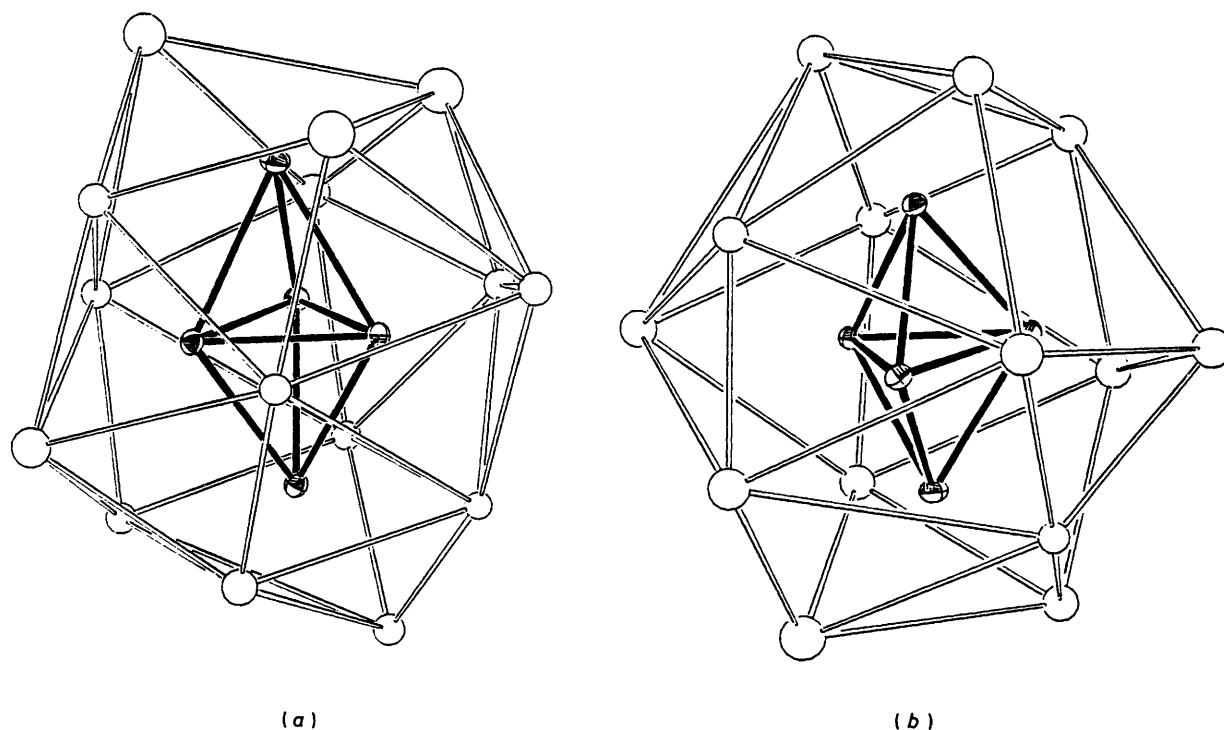


Figure 4. Polyhedra formed by the oxygen atoms of the ligands in (a) $[\text{FeIr}_4(\text{CO})_{15}]^{2-}$ and (b) $[\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]^-$

Table 3. Summary of crystal data and intensity collection parameters for compounds (1) and (2)^a

Compound	$[\text{N}(\text{PPh}_3)_2]_2^-$ $[\text{FeIr}_4(\text{CO})_{15}] \cdot 2\text{C}_4\text{H}_8\text{O}$	$[\text{PPh}_4][\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]^-$
Formula	$\text{C}_{95}\text{H}_{76}\text{FeIr}_4\text{N}_2\text{O}_{17}\text{P}_4$	$\text{C}_{38}\text{H}_{20}\text{Fe}_2\text{Ir}_3\text{O}_{14}\text{P}$
<i>M</i>	2 466.81	1 419.84
System	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
<i>a</i> /Å	11.399(3)	12.461(5)
<i>b</i> /Å	14.032(3)	14.306(5)
<i>c</i> /Å	29.163(4)	23.504(6)
α /°	86.18(2)	
β /°	84.52(2)	
γ /°	80.14(2)	
<i>U</i> /Å ³	4 569(2)	4 190(4)
<i>Z</i>	2	4
<i>D_c</i> /g cm ⁻³	1.793	2.251
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	60.71	102.36
ω scan width/°	$1.20 + 0.35 \tan \theta$	$1.80 + 0.35 \tan \theta$
Octants in the reciprocal space explored	$\pm h, \pm k, \pm l$	$+h, +k, +l$
Measured reflections	9 719	4 100
Unique observed reflections [<i>I</i> > 3 σ (<i>I</i>)]	3 985	2 752
Final <i>R</i> , <i>R'</i> ^b	0.042, 0.045	0.032, 0.040
No. of variables	538	263
Min. transmission factor	0.92	0.63
E.s.d. ^c	1.290	0.982

^a Details common to both compounds: scan mode, ω ; θ range 3–25°. ^b $R = [\sum(F_o - k|F_c|)/\sum F_o]$; $R' = [\sum w(F_o - k|F_c|)^2/\sum wF_o^2]^{1/2}$. ^c e.s.d. = $[\sum w(F_o - k|F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o , N_v = number of observations and number of variables, respectively.

$[\text{Fe}(\text{CO})_5]$ (0.150 cm³, 1.1 mmol) was added with a microsyringe and the mixture vigorously stirred. After 4–8 h the i.r. spectrum showed essentially the bands of $\text{Na}_2[\text{FeIr}_4(\text{CO})_{15}]$ (2 016s, 1 974vs, 1 800mw, and 1 765mw cm⁻¹). The salt $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ (1.43 g, 2.5 mmol) in MeOH (15 cm³) was added resulting in the formation of a yellow precipitate which was collected by filtration, washed with MeOH (2 × 10 cm³), water (5 × 10 cm³), and 2-propanol (2 × 10 cm³), and vacuum dried. The yellow product obtained was fairly pure according to i.r. spectroscopy. It can be recrystallized by the slow diffusion of 2-propanol (40 cm³) into a thf solution (15 cm³). In this case a crystalline sample of $[\text{N}(\text{PPh}_3)_2]_2[\text{FeIr}_4(\text{CO})_{15}] \cdot 2\text{C}_4\text{H}_8\text{O}$ is obtained but with lower yields due to partial decomposition into soluble by-products. Yield 1.073 g (43%) (Found: C, 44.9; H, 2.8; N, 1.7. Calc. for $\text{C}_{95}\text{H}_{76}\text{FeIr}_4\text{N}_2\text{O}_{17}\text{P}_4$: C, 46.3; H, 3.1; N, 1.15%). It should be noted that prolonged vacuum drying can remove some clathrated thf.

Preparation of $[\text{PPh}_4][\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]^-$ (2).—In a Schlenk tube were placed $\text{Na}_2[\text{Fe}(\text{CO})_4]$ (0.067 g, 0.31 mmol), $[\text{PPh}_4][\text{Ir}(\text{CO})_2\text{Cl}_2]$ (0.31 g, 0.47 mmol), and thf (10 cm³). The mixture was stirred for 12 h at room temperature then the solvent was removed *in vacuo*. The crude residue was suspended in methanol (15 cm³) and after 6 h the colourless precipitate was eliminated by filtration. To the red solution were added $[\text{PPh}_4]\text{Br}$ (0.20 g) and water (30 cm³). The flaky precipitate was then filtered off, dried, and extracted from the frit with thf (10 cm³). This solution was concentrated to a small volume (3–5 cm³) and cyclohexane layered upon it. By slow diffusion well shaped prismatic crystals of (2) were obtained. Yield 0.090 g, (40%) (Found: C, 33.4; H, 1.7. Calc. for $\text{C}_{38}\text{H}_{20}\text{Fe}_2\text{Ir}_3\text{O}_{14}\text{P}$: C, 32.1; H, 1.4%).

Crystallography for Complexes (1) and (2).—Collection and reduction of the X-ray data. The crystal data for compounds (1) and (2) are summarized in Table 3 together with some experi-

Table 4. Fractional atomic co-ordinates for the complex $[\text{N}(\text{PPh}_3)_2]_2[\text{FeIr}_4(\text{CO})_{15}]$ with e.s.d.s in parentheses*

Atom	x	y	z	Atom	x	y	z
Ir(1)	0.570 55(8)	0.290 38(7)	-0.279 22(3)	C(214)	0.601(2)	-0.410(2)	-0.004 3(8)
Ir(2)	0.535 37(8)	0.190 71(6)	-0.196 92(3)	C(215)	0.545(2)	-0.358(1)	0.032 7(7)
Ir(3)	0.391 35(8)	0.357 94(6)	-0.215 30(3)	C(216)	0.448(2)	-0.283(1)	0.024 1(7)
Ir(4)	0.361 87(9)	0.187 56(7)	-0.267 72(4)	C(221)	0.146(2)	-0.206(1)	0.009 7(6)
Fe	0.639 0(3)	0.369 4(2)	-0.197 2(1)	C(222)	0.156(2)	-0.285(1)	0.040 9(7)
O(1)	0.720(1)	0.446(1)	-0.120 0(5)	C(223)	0.049(2)	-0.301(1)	0.070 9(7)
O(2)	0.877(1)	0.281(1)	-0.233 5(6)	C(224)	-0.056(2)	-0.233(1)	0.064 7(7)
O(3)	0.656(1)	0.533(1)	-0.262 9(5)	C(225)	-0.065(2)	-0.155(1)	0.033 8(7)
O(11)	0.752(2)	0.359(1)	-0.344 9(7)	C(226)	0.039(2)	-0.141(1)	0.005 0(7)
O(21)	0.550(1)	-0.007(1)	-0.153 1(6)	C(231)	0.305(2)	-0.065(1)	-0.011 3(6)
O(31)	0.141(2)	0.460(1)	-0.199 0(6)	C(232)	0.358(2)	-0.006(1)	-0.046 6(7)
O(41)	0.477(2)	-0.019(2)	-0.275 3(8)	C(233)	0.383(2)	0.084(1)	-0.030 5(7)
O(42)	0.184(2)	0.165(2)	-0.188 8(8)	C(234)	-0.357(2)	-0.110(1)	-0.014 4(7)
O(43)	0.184(2)	0.282(1)	-0.334 3(8)	C(235)	-0.305(2)	-0.051(1)	-0.048 3(7)
OD(2)	0.686(1)	0.216 8(9)	-0.124 0(5)	C(236)	0.278(2)	-0.040(1)	0.034 5(7)
OD(3)	0.435(1)	0.500(1)	-0.150 9(5)	C(311)	0.055(2)	-0.077(1)	-0.481 4(7)
OD(12)	0.742(1)	0.102(1)	-0.262 2(5)	C(312)	0.156(2)	-0.287(2)	-0.507 3(8)
OD(13)	0.404(1)	0.479(1)	-0.306 5(5)	C(313)	0.144(2)	-0.314(2)	-0.554 0(9)
OD(14)	0.513(1)	0.200(1)	-0.357 7(6)	C(314)	0.034(2)	-0.290(2)	-0.569 6(9)
OD(23)	0.336(1)	0.254(1)	-0.123 1(5)	C(315)	-0.064(2)	-0.238(2)	-0.545 0(8)
C(1)	0.686(2)	0.415(1)	-0.151 0(7)	C(316)	-0.056(2)	-0.212(1)	-0.499 8(7)
C(2)	0.777(2)	0.315(2)	-0.221 7(9)	C(321)	0.055(2)	-0.320(1)	-0.388 4(7)
C(3)	0.642(2)	0.465(2)	-0.238 2(8)	C(322)	0.130(2)	-0.359(2)	-0.356 7(8)
C(11)	0.673(2)	0.332(2)	-0.321(1)	C(323)	0.105(2)	-0.445(2)	-0.330 8(9)
C(21)	0.542(2)	0.074(2)	-0.169 4(8)	C(324)	0.011(2)	-0.487(2)	-0.339 1(9)
C(31)	0.245(2)	0.418(2)	-0.206 9(9)	C(325)	-0.056(2)	-0.450(2)	-0.371 3(8)
C(41)	0.428(3)	0.064(2)	-0.269(1)	C(326)	-0.039(2)	-0.365(2)	-0.397 7(8)
C(42)	0.250(3)	0.173(2)	-0.219(1)	C(331)	-0.039(2)	-0.114(1)	-0.404 6(7)
C(43)	0.247(2)	0.253(2)	-0.305(1)	C(332)	-0.050(2)	-0.031(1)	-0.431 7(7)
CD(2)	0.636(2)	0.249(1)	-0.157 9(7)	C(333)	-0.135(2)	0.051(2)	-0.416 1(9)
CD(3)	0.472(2)	0.438(1)	-0.175 8(7)	C(334)	-0.196(2)	0.044(2)	-0.376 2(8)
CD(12)	0.655(2)	0.165(1)	-0.252 5(7)	C(335)	-0.186(2)	-0.042(2)	-0.345 1(8)
CD(13)	0.439(2)	0.410(1)	-0.280 5(8)	C(336)	-0.098(2)	-0.123(2)	-0.361 2(8)
CD(14)	0.487(2)	0.219(2)	-0.316 1(8)	C(411)	0.201(2)	-0.062(1)	-0.349 9(7)
CD(23)	0.387(2)	0.259(2)	-0.161 5(8)	C(412)	0.129(2)	0.028(1)	-0.353 9(7)
P(1)	0.170 5(5)	-0.207 2(4)	-0.114 2(2)	C(413)	0.062(2)	0.072(1)	-0.315 1(7)
P(2)	0.272 7(5)	-0.179 5(4)	-0.027 9(2)	C(414)	0.072(2)	0.021(2)	-0.272 7(9)
P(3)	0.077 6(5)	-0.212 2(4)	-0.422 7(2)	C(415)	0.142(2)	-0.066(2)	-0.266 9(9)
P(4)	0.278 2(5)	-0.120 4(4)	-0.398 3(2)	C(416)	0.210(2)	-0.110(1)	-0.306 2(8)
N(1)	0.247(1)	-0.166(1)	-0.080 2(6)	C(421)	0.414(2)	-0.191(1)	-0.383 4(7)
N(2)	0.211(1)	-0.190(1)	-0.421 0(6)	C(422)	0.439(2)	-0.289(2)	-0.391 8(8)
C(111)	0.054(1)	-0.111(1)	-0.132 1(6)	C(423)	0.544(2)	-0.348(2)	-0.377(1)
C(112)	-0.032(2)	-0.135(1)	-0.159 7(8)	C(424)	0.625(2)	-0.304(2)	-0.356 9(8)
C(113)	0.120(2)	0.058(1)	0.174 9(8)	C(425)	0.605(2)	-0.209(2)	-0.348 8(8)
C(114)	0.124(2)	-0.035(1)	0.161 5(7)	C(426)	0.493(2)	-0.149(2)	-0.361 0(9)
C(115)	0.042(2)	-0.057(1)	0.134 4(7)	C(431)	0.319(2)	-0.025(1)	-0.438 3(7)
C(116)	0.050(2)	-0.016(1)	-0.118 8(6)	C(432)	0.364(2)	0.053(2)	-0.421 8(8)
C(121)	0.265(2)	-0.244(1)	-0.165 7(6)	C(433)	0.397(2)	0.122(2)	-0.457 5(8)
C(122)	0.288(2)	-0.310(1)	-0.194 1(7)	C(434)	0.381(2)	0.117(1)	-0.503 4(7)
C(123)	-0.306(2)	0.338(1)	0.234 6(8)	C(435)	0.337(2)	0.040(1)	-0.518 2(7)
C(124)	-0.404(2)	0.296(2)	0.245 3(8)	C(436)	0.302(2)	-0.034(1)	-0.486 4(8)
C(125)	0.436(2)	-0.233(2)	-0.218 1(8)	OS(1)	0.242(2)	0.252(2)	0.221 3(9)
C(126)	-0.369(2)	0.203(1)	0.175 8(8)	CS(1)	0.247(3)	0.320(2)	0.176(1)
C(131)	0.097(2)	-0.306(1)	-0.090 5(7)	CS(2)	0.134(3)	0.389(2)	0.188(1)
C(132)	0.167(2)	-0.401(1)	-0.092 7(8)	CS(3)	0.067(3)	0.351(2)	0.224(1)
C(133)	-0.107(2)	0.479(2)	0.072 9(8)	CS(4)	0.133(3)	0.280(2)	0.248(1)
C(134)	0.012(2)	0.460(2)	0.054 1(8)	OS(2)	0.430(3)	0.378(2)	0.512(1)
C(135)	0.074(2)	0.369(2)	0.052 5(8)	CS(5)	0.300(4)	0.418(3)	0.504(2)
C(136)	0.020(2)	0.290(1)	0.072 5(7)	CS(6)	0.485(4)	0.392(3)	0.558(2)
C(211)	0.399(1)	-0.270(1)	-0.018 7(6)	CS(7)	0.372(4)	0.441(3)	0.576(2)
C(212)	0.454(2)	-0.323(1)	-0.054 5(7)	CS(8)	0.264(4)	0.448(3)	0.551(1)
C(213)	0.556(2)	-0.395(1)	-0.047 6(8)				

* D refers to atoms of edge-bridging carbonyls, S to atoms of clathrated solvent molecules.

mental details. The dianions $[\text{RuRh}_4(\text{CO})_{15}]^{2-}$,¹⁰ $[\text{FeRh}_4(\text{CO})_{15}]^{2-}$,⁹ and $[\text{RuIr}_4(\text{CO})_{15}]^{2-}$,¹⁴ as their $[\text{N}(\text{PPh}_3)_2]^+$ salts, are isomorphous. The $[\text{N}(\text{PPh}_3)_2]^+$ salt of (1) contains two clathrated molecules of thf and its cell parameters are slightly larger.

Crystals of the two compounds were mounted in an arbitrary orientation on a glass fibre which was then fixed into an aluminium pin and mounted onto a goniometer head. Diffraction data were collected on an Enraf-Nonius CAD4 automated diffractometer, controlled by a PDP 11/73

Table 5. Fractional atomic co-ordinates for the complex $[\text{PPh}_4][\text{Fe}_2\text{Ir}_3(\text{CO})_{14}]$ with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Ir(1)	0.060 71(5)	0.836 84(5)	0.067 25(3)	C(52)	0.018(2)	0.603(1)	0.107 9(8)
Ir(2)	-0.145 67(5)	0.843 23(5)	0.096 51(3)	CD(14)	0.043(2)	0.963(1)	0.024 0(8)
Ir(3)	0.008 94(6)	0.876 52(5)	0.176 97(3)	CD(25)	-0.161(1)	0.702(1)	0.093 2(8)
Fe(4)	-0.023 1(2)	0.998 5(2)	0.095 4(1)	CD(34)	-0.085(2)	1.005(1)	0.168 4(8)
Fe(5)	-0.028 4(2)	0.708 2(2)	0.137 5(1)	CD(35)	0.100(1)	0.740(1)	0.170 5(7)
P	0.486 9(4)	0.750 3(3)	0.334 0(2)	C(111)	0.579(1)	0.849(1)	0.339 5(7)
O(11)	0.044(1)	0.706(1)	-0.032 3(6)	C(112)	0.623(2)	0.868(2)	0.390 3(9)
O(12)	0.304(1)	0.840(1)	0.075 5(7)	C(113)	0.693(2)	0.945(2)	0.394(1)
O(21)	-0.230(1)	0.875(1)	-0.021 7(6)	C(114)	0.714(2)	0.997(2)	0.350(1)
O(22)	-0.351(1)	0.893(1)	0.157 2(7)	C(115)	0.667(2)	0.978(2)	0.297 7(9)
O(31)	-0.102(1)	0.839(1)	0.287 9(7)	C(116)	0.599(1)	0.898(1)	0.294 5(8)
O(32)	0.224(1)	0.948(1)	0.216 2(7)	C(121)	0.520(2)	0.664(1)	0.385 9(8)
O(41)	0.112(1)	1.159(1)	0.114 7(7)	C(122)	0.440(2)	0.617(2)	0.414 7(9)
O(42)	-0.182(1)	1.114(1)	0.038 9(6)	C(123)	0.468(2)	0.554(2)	0.457(1)
O(51)	-0.119(2)	0.622(1)	0.236 0(8)	C(124)	0.567(2)	0.527(2)	0.466(1)
O(52)	0.047(1)	0.537(1)	0.085 1(6)	C(125)	0.652(2)	0.576(2)	0.442(1)
OD(14)	0.062(1)	0.988(1)	-0.021 4(6)	C(126)	0.626(2)	0.648(2)	0.401(1)
OD(25)	-0.215(1)	0.646(1)	0.070 5(6)	C(131)	0.352(1)	0.791(1)	0.344 1(7)
OD(34)	-0.136(1)	1.048(1)	0.203 0(6)	C(132)	0.265(1)	0.740(1)	0.324 9(7)
OD(35)	0.184(1)	0.718(1)	0.190 2(5)	C(133)	0.162(2)	0.769(1)	0.337 5(8)
C(11)	0.049(1)	0.756(1)	0.006 8(8)	C(134)	0.145(2)	0.850(2)	0.369 2(8)
C(12)	0.208(2)	0.835(1)	0.070 9(8)	C(135)	0.234(2)	0.900(1)	0.388 5(8)
C(21)	-0.196(2)	0.865(1)	0.025 2(8)	C(136)	0.337(1)	0.870(1)	0.375 3(8)
C(22)	-0.273(2)	0.872(1)	0.135 4(8)	C(141)	0.502(1)	0.700(1)	0.264 3(7)
C(31)	-0.056(2)	0.858(2)	0.246 7(9)	C(142)	0.582(2)	0.631(2)	0.256 8(9)
C(32)	0.138(2)	0.922(2)	0.204(1)	C(143)	0.602(2)	0.600(2)	0.200 2(9)
C(41)	0.068(2)	1.091(1)	0.103 7(9)	C(144)	0.542(2)	0.635(2)	0.158(1)
C(42)	-0.117(1)	1.065(1)	0.062 6(8)	C(145)	0.466(2)	0.702(1)	0.163 5(9)
C(51)	-0.083(2)	0.654(2)	0.196 9(9)	C(146)	0.443(1)	0.735(1)	0.218 1(8)

computer, using Mo- K_α radiation ($\lambda = 0.710 73 \text{ \AA}$) with a graphite crystal monochromator in the incident beam. The Enraf-Nonius program SEARCH was employed to obtain 25 accurately centred reflections which were then used in the program INDEX to obtain an orientation matrix for data collection and to provide cell dimensions.³⁶ A periodic remeasurement of three standard reflections revealed a crystal decay, on X-ray exposure, which was evaluated as about 15% for (1) and 10% for (2) on F_0 at the end of the data collection. Lorentz, polarization, decay, and absorption corrections were applied, the latter performed with the empirical method described in ref. 37.

Solution and refinement of the structures. The Ir and the Fe atoms were located from a three-dimensional Patterson map, and the co-ordinates of the remaining non-hydrogen atoms located by successive least-squares refinements and Fourier difference maps. The refinement was carried out by full-matrix least squares with anisotropic thermal parameters for Ir, Fe, and P for both compounds while the light atoms were refined isotropically. The function minimized was $\sum w(F_o - k|F_c|)^2$. Individual weights were $w = 1/\sigma^2(F_o)$ where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{1/2}/L_p$ and p the 'ignorance factor' = 0.04 for both compounds. Scattering factors and anomalous dispersion corrections were taken from ref. 38. The positional parameters for compounds (1) and (2) are listed in Tables 4 and 5, respectively.

The chirality of the crystals of compound (2) was tested by refining both enantiomorphous structures.³⁹ The fractional atomic co-ordinates reported in Table 5 refer to the enantiomer with the lower R and R' values: 0.032 vs. 0.041 and 0.046 vs. 0.058, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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