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SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF $[PPN]^+_2[RuIr_4(CO)_9(\mu_2\text{-}CO)_6]^{2-}$ *

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Summary

The dianion $[RuIr_4(CO)_{15}]^{2-}$ has been obtained by reductive carbonylation of mixtures of $Ir_4(CO)_{12}$ and $RuCl_3 \cdot x\ H_2O$, and the bis(triphenylphosphine)-iminium salt has been characterized by single-crystal X-ray diffraction techniques. Crystal data: $[((C_6H_5)_3P)_2N]_2[RuIr_4(CO)_{15}]$, space group $P\bar{1}$ ($Z = 2$), $a = 11.425(3)$, $b = 14.141(2)$, $c = 25.979(5)$ Å, $\alpha = 84.55(1)$, $\beta = 83.53(2)$, $\gamma = 82.71(2)°$. The mixed-metal cluster has a structure with an elongated trigonal bipyramidal array of metal atoms in which Ru occupies an apical position. The anion is unstable in vacuum or in an N_2 atmosphere yielding predominantly another mixed-metal species which is not as yet fully characterized. Upon reexposure to CO, this latter species is converted back to $[RuIr_4(CO)_{15}]^{2-}$, plus additional products.

Introduction

Until two years ago pentanuclear metal cluster compounds seemed to be rather uncommon, but since that time the number of such species known has almost doubled. At present, at least a dozen with trigonal bipyramidal geometry have been indentified and structures of the majority of these have been determined [1—7]. The trigonal bipyramidal dianion $[RuIr_4(CO)_{15}]^{2-}$ reported here

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is closely related the members of the series $[MRh_4(CO)_{14}]^{2-}$, M = Ni, Pt [6,7]. These species have common structural features and the same number of valence electrons (76), and also possess similar chemical reactivity.

Results

The novel mixed-metal pentanuclear cluster $[RuIr_4(CO)_{15}]^{2-}$ has been isolated among the products obtained by reductive carbonylation of mixtures of $Ir_4(CO)_{12}$ and $RuCl_3 \cdot x\ H_2O$ or $Ru_3(CO)_{12}$ over a range of Ru : Ir ratios. The reactions were carried out with NaOH in MeOH * under a CO atmosphere.

Some compenents of these reaction mixtures were separated by fractional crystallization after precipitation with a bulky cation (usually PPN). In this way it was possible to recover and later identify three principal products: $[HIr_4(CO)_{11}]^-$, $[Ir_6(CO)_{15}]^{2-}$ and $[RuIr_4(CO)_{15}]^{2-}$ **. The relative amounts of these species depended mainly on the severity of the reduction (i.e. the concentration of NaOH) and the Ru : Ir ratio. Under mild reducing conditions (NaOH less than 0.5 *M* with $Ir_4(CO)_{12}$ 0.01—0.03 *M* *** and $RuCl_3$ 0.01—0.10 *M*) the tetranuclear hydrido species was the most abundant product recovered by precipitation. Under these conditions small amounts of $[Ir_6(CO)_{15}]^{2-}$ were also detected, while the Ru apparently gave unidentified species which were not precipitated by adding [PPN]Cl and H_2O.

Highly reducing concentrations of NaOH (1—2 *M*) were required for production of the mixed-metal dianion $[RuIr_4(CO)_{15}]^{2-}$. However, with the ideal stoichiometric ratio Ru : Ir of 1 : 4 this species was recovered from the crude product in less than 10% yield estimated relative to the $Ir_4(CO)_{12}$ reacted. The remainder of the product was identified by IR as $[HIr_4(CO)_{11}]^-$ and $[Ir_6(CO)_{15}]^{2-}$. More substantial amounts of the $RuIr_4$ species were obtained (up to 30%) in reactions employing $RuCl_3 \cdot x\ H_2O$ in up to eight-fold excess of the ideal stoichiometry. With $Ru_3(CO)_{12}$ as a starting material, poorer yields were obtained.

It was necessary to perform all the successive manipulations of the crude product under CO. In fact, if recrystallization was performed under N_2, black crystals were obtained together with the orange crystals of $[PPN]_2[RuIr_4(CO)_{15}]$. The pure product was obtained by recrystallization under CO, and storage under CO was also required to prevent slow decomposition which occurred in N_2, particularly with finely powdered material.

The IR spectrum of $[RuIr_4(CO)_{15}]^{2-}$ (PPN salt in THF) shown in Fig. 1 is quite characteristic and reminiscent of other pentanuclear species, consisting essentially of two strong bands in the terminal CO and two medium-strong bands in the bridging region. The yellow THF solutions became darker upon standing in N_2 atmosphere. This process could be facilitated by performing a few cycles evacuation to dryness and redissolution, or more simply maintaining a renewed static vacuum for about 1/2 h. The solutions ultimately became brown, and this progressive transformation could be followed by IR. When the

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* Abbreviations: MeOH methanol, PPN bis(triphenylphosphine) iminium, THF tetrahydrofuran.

** The first two species have previously been reported by Malatesta and coworkers [8].

*** $Ir_4(CO)_{12}$ is insoluble in MeOH; these values should be construed as moles of $Ir_4(CO)_{12}$ reacted/volume of MeOH used in a particular reaction.

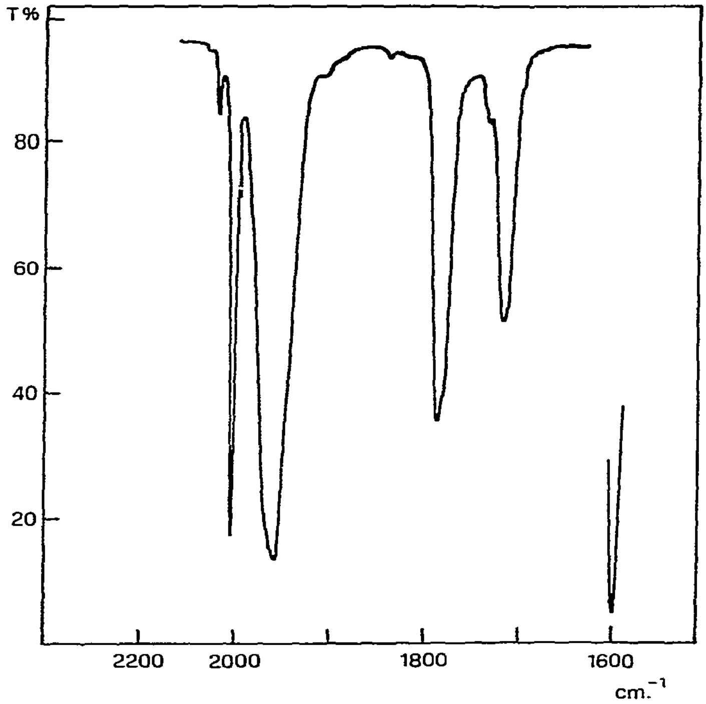

Fig. 1. IR spectrum of $[PPN]_2[RuIr_4(CO)_{15}]$ in THF; bands at 2031w, 2015s, 1965(sh), 1960s, 1791ms, 1786(sh), 1726m (w = weak, s = strong, sh = shoulder, m = medium). Polystyrene (1601) was employed as a standard.

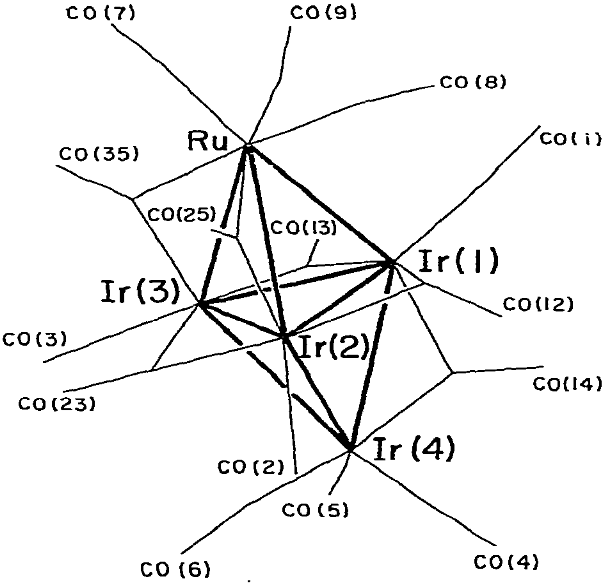

Fig. 2. View of $[RuIr_4(CO)_{15}]^{2-}$ showing the atom-numbering scheme.

characteristic bands of $[RuIr_4(CO)_{15}]^{2-}$ had disappeared, the spectra presented a rather complex pattern consistent with the presence of additional compounds, although a single species appeared to be most abundant. Crystallization

TABLE 1

BOND DISTANCES (Å)

(a) $[RuIr_4(CO)_{15}]^{2-}$

Metal—metal		*Metal—C (bridging)*	
Ru—Ir(1)	2.957(5)	Ru—C(25)	2.11(6)
Ru—Ir(2)	3.034(5)	Ru—C(35)	2.12(4)
Ru—Ir(3)	3.046(4)		
Ir(1)—Ir(2)	2.727)3)	mean	2.12(1)
Ir(1)—Ir(3)	2.715(3)		
Ir(1)—Ir(4)	2.963(3)		
Ir(2)—Ir(3)	2.694(3)	Ir(1)—C(12)	1.86(8)
Ir(2)—Ir(4)	3.007(3)	Ir(1)—C(13)	2.04(5)
Ir(3)—Ir(4)	3.038(3)	Ir(1)—C(14)	1.99(4)
		Ir(2)—C(12)	2.04(8)
		Ir(2)—C(23)	2.04(5)
Metal—C (terminal)		Ir(2)—C(25)	1.94(7)
Ru—C(7)	1.83(6)	Ir(3)—C(13)	1.98(5)
Ru—C(8)	1.90(5)	Ir(3)—C(23)	2.05(5)
Ru—C(9)	1.86(4)	Ir(3)—C(35)	1.97(5)
		Ir(4)—C(14)	1.86(3)
mean	1.86(2)		
		mean	1.98(2)
Ir(1)—C(1)	1.68(5)		
Ir(2)—C(2)	1.73(4)	*C—O (terminal)*	
Ir(3)—C(3)	1.75(5)	C(1)—O(1)	1.22(6)
Ir(4)—C(4)	1.62(7)	C(2)—O(2)	1.33(6)
Ir(4)—C(5)	1.82(6)	C(3)—O(3)	1.32(6)
Ir(4)—C(6)	1.65(7)	C(4)—O(4)	1.35(8)
		C(5)—O(5)	1.17(8)
mean	1.71(3)	C(6)—O(6)	1.33(8)
		C(7)—O(7)	1.21(7)
		C(8)—O(8)	1.18(6)
		C(9)—O(9)	1.22(6)
		mean	1,26(2)
		C—O (bridging)	
		C(12)—O(12)	1.56(9)
		C(13)—O(13)	1.33(6)
		C(14)—O(14)	1.33(5)
		C(23)—O(23)	1.27(6)
		C(25)—O(25)	1.20(7)
		C(35)—O(35)	1.20(6)
		mean	1.32(5)

(b) PPN

Cation 1		*Cation 2*	
P(11)—N(1)	1.64(4)	P(21)—N(2)	1.59(3)
P(12)—N(1)	1.54(3)	P(22)—N(2)	1.60(3)
P—C [a]	1.82(1)	P—C [a]	1.80(1)
C—C [a]	1.39(1)	C—C [a]	1.41(1)

[a] Mean values.

TABLE 2

BOND ANGLES (°)

(a) $[RuIr_4(CO)_{15}]^{2-}$

Metal—metal—metal		*Metal—metal—C (terminal)*	
Ir(1)—Ru—Ir(2)	54.14(9)	Ir(1)—Ru—C(7)	175(2)
Ir(1)—Ru—Ir(3)	53.76(9)	Ir(1)—Ru—C(8)	87(2)
Ir(2)—Tu—Ir(3)	52.61(8)	Ir(1)—Ru—C(9)	79(2)
Ru—Ir(1)—Ir(2)	64.4(1)	Ir(2)—Ru—C(7)	127(2)
Ru—Ir(1)—Ir(3)	64.79(9)	Ir(2)—Ru—C(8)	96(2)
Ru—Ir(1)—Ir(4)	120.2(1)	Ir(2)—Ru—C(9)	131(2)
Ir(2)—Ir(1)—Ir(3)	59.34(7)	Ir(3)—Ru—C(7)	131(2)
Ir(2)—Ir(1)—Ir(4)	63.65(7)	Ir(3)—Ru—C(8)	139(2)
Ir(3)—Ir(1)—Ir(4)	64.53(7)	Ir(3)—Ru—C(9)	91(1)
Ru—Ir(2)—Ir(1)	61.50(9)	Ru—Ir(1)—C(1)	98(2)
Ru—Ir(2)—Ir(3)	63.93(9)	Ir(2)—Ir(1)—C(1)	145(2)
Ru—Ir(2)—Ir(4)	116.3(1)	Ir(3)—Ir(1)—C(1)	143(2)
Ir(1)—Ir(2)—Ir(3)	60.11(7)	Ir(4)—Ir(1)—C(1)	142(2)
Ir(1)—Ir(2)—Ir(4)	62.00(7)	Ru—Ir(2)—C(2)	142(1)
Ir(3)—Ir(2)—Ir(4)	64.13(7)	Ir(1)—Ir(2)—C(2)	144(1)
Ru—Ir(3)—Ir(1)	61.45(9)	Ir(3)—Ir(2)—C(2)	145(1)
Ru—Ir(3)—Ir(2)	63.46(9)	Ir(4)—Ir(2)—C(2)	101(1)
Ru—Ir(3)—Ir(4)	115.0(1)	Ru—Ir(3)—C(3)	139(2)
Ir(1)—Ir(3)—Ir(2)	60.55(7)	Ir(1)—Ir(3)—C(3)	148(2)
Ir(1)—Ir(3)—Ir(4)	61.69(7)	Ir(2)—Ir(3)—C(3)	144(2)
Ir(2)—Ir(3)—Ir(4)	62.95(7)	Ir(4)—Ir(3)—C(3)	106(2)
Ir(1)—Ir(4)—Ir(2)	54.36(7)	Ir(1)—Ir(4)—C(4)	108(2)
Ir(1)—Ir(4)—Ir(3)	53.78(6)	Ir(1)—Ir(4)—C(5)	107(2)
Ir(2)—Ir(4)—Ir(3)	52.92(6)	Ir(1)—Ir(4)—C(6)	128(3)
		Ir(2)—Ir(4)—C(4)	94(2)
		Ir(2)—Ir(4)—C(5)	149(2)
		Ir(2)—Ir(4)—C(6)	82(3)
		Ir(3)—Ir(4)—C(4)	147(2)
		Ir(3)—Ir(4)—C(5)	96(2)
		Ir(3)—Ir(4)—C(6)	79(3)
Metal—metal—C (bridging)		*C—metal—C*	
Ir(1)—Ru—C(25)	90(2)	C(7)—Ru—C(8)	88(2)
Ir(1)—Ru—C(35)	92(1)	C(7)—Ru—C(9)	101(2)
Ir(2)—Ru—C(25)	39(1)	C(7)—Ru—C(25)	90(2)
Ir(2)—Ru—C(35)	83(1)	C(7)—Ru—C(35)	93(2)
Ir(3)—Ru—C(25)	84(2)	C(8)—Ru—C(9)	93(2)
Ir(3)—Ru—C(35)	40(1)	C(8)—Ru—C(25)	84(2)
Ru—Ir(1)—C(12)	77(3)	C(8)—Ru—C(35)	179(2)
Ru—Ir(1)—C(13)	90(2)	C(9)—Ru—C(25)	169(2)
Ru—Ir(1)—C(14)	158(1)	C(25)—Ru—C(35)	96(2)
Ir(2)—Ir(1)—C(12)	48(2)	C(1)—Ir(1)—C(12)	100(3)
Ir(2)—Ir(1)—C(13)	105(2)	C(1)—Ir(1)—C(13)	105(2)
Ir(2)—Ir(1)—C(14)	95(1)	C(1)—Ir(1)—C(14)	104(2)
Ir(3)—Ir(1)—C(12)	107(2)	C(12)—Ir(1)—C(13)	153(3)
Ir(3)—Ir(1)—C(13)	46(2)	C(12)—Ir(1)—C(14)	96(3)
Ir(3)—Ir(1)—C(14)	98(1)	C(13)—Ir(1)—C(14)	87(2)
Ir(4)—Ir(1)—C(12)	89(3)	C(2)—Ir(2)—C(12)	108(3)
Ir(4)—Ir(1)—C(13)	77(2)	C(2)—Ir(2)—C(23)	100(2)
Ir(4)—Ir(1)—C(14)	38(1)	C(2)—Ir(2)—C(25)	99(2)
Ru—Ir(2)—C(12)	73(3)	C(12)—Ir(2)—C(23)	151(3)
Ru—Ir(2)—C(23)	89(2)	C(12)—Ir(2)—C(25)	90(3)
Ru—Ir(2)—C(25)	44(2)	C(23)—Ir(2)—C(25)	92(2)
Ir(1)—Ir(2)—C(12)	43(2)	C(3)—Ir(3)—C(13)	101(2)
Ir(1)—Ir(2)—C(23)	109(1)	C(3)—Ir(3)—C(23)	97(2)
Ir(1)—Ir(2)—C(25)	102(2)	C(3)—Ir(3)—C(35)	95(2)
Ir(3)—Ir(2)—C(12)	103(2)	C(13)—Ir(3)—C(23)	154(2)

TABLE 2 (continued)

Metal—metal—C (bridging)		*C—metal—C*	
Ir(3)—Ir(2)—C(23)	49(1)	C(13)—Ir(3)—C(35)	108(2)
Ir(3)—Ir(2)—C(25)	98(2)	C(23)—Ir(3)—C(35)	88(2)
Ir(4)—Ir(2)—C(12)	85(2)	C(4)—Ir(4)—C(5)	116(3)
Ir(4)—Ir(2)—C(23)	83(2)	C(4)—Ir(4)—C(6)	101(3)
Ir(4)—Ir(2)—C(25)	160(2)	C(4)—Ir(4)—C(14)	86(3)
Ru—Ir(3)—C(13)	89(2)	C(5)—Ir(4)—C(6)	97(3)
Ru—Ir(3)—C(23)	89(1)	C(5)—Ir(4)—C(14)	87(2)
Ru—Ir(3)—C(35)	44(1)	C(6)—Ir(4)—C(14)	169(3)
Ir(1)—Ir(3)—C(13)	48(2)		
Ir(1)—Ir(3)—C(23)	109(1)		
Ir(1)—Ir(3)—C(35)	103(1)	*Metal—C—metal*	
Ir(2)—Ir(3)—C(13)	108(2)	Ir(1)—C(12)—Ir(2)	89(3)
Ir(2)—Ir(3)—C(23)	49(1)	Ir(1)—C(13)—Ir(3)	85(2)
Ir(2)—Ir(3)—C(35)	95(1)	Ir(1)—C(14)—Ir(4)	101(2)
Ir(4)—Ir(3)—C(13)	76(2)	Ir(2)—C(23)—Ir(3)	82(2)
Ir(4)—Ir(3)—C(23)	82(2)	Ru—C(25)—Ir(2)	97(3)
Ir(4)—Ir(3)—C(35)	157(1)	Ru—C(35)—Ir(3)	96(2)
Ir(1)—Ir(4)—C(14)	41(1)		
Ir(2)—Ir(4)—C(14)	90(1)		
Ir(3)—Ir(4)—C(14)	91(1)		
metal—C—O (bridging)		*Metal—C—O (terminal)*	
Ir(1)—C(12)—O(12)	137(6)		
Ir(2)—C(12)—O(12)	118(5)	Ir(1)—C(1)—O(1)	172(4)
Ir(1)—C(13)—O(13)	132(4)	Ir(2)—C(2)—O(2)	176(4)
Ir(3)—C(13)—O(13)	142(4)	Ir(3)—C(3)—O(3)	175(4)
Ir(1)—C(14)—O(14)	116(3)	Ir(4)—C(4)—O(4)	175(6)
Ir(4)—C(14)—O(14)	143(3)	Ir(4)—C(5)—O(5)	170(6)
Ir(3)—C(23)—O(23)	138(4)	Ir(4)—C(6)—O(6)	167(6)
Ru—C(25)—O(25)	131(5)	Ru—C(7)—O(7)	176(4)
Ir(2)—C(25)—O(25)	132(5)	Ru—C(8)—O(8)	167(5)
Ru—C(35)—O(35)	131(4)	Ru—C(9)—O(9)	170(4)
Ir(3)—C(35)—O(35)	131(4)		
(b) PPN			
Cation 1		*Cation 2*	
P(11)—N(1)—P(12)	136(2)	P(21)—N(2)—P(22)	135(2)
N—P—C ^{a}	111(2)	N—P—C ^{a}	111(1)
C—P—C ^{a}	108(1)	C—P—C ^{a}	108(1)
P—C—C ^{a}	118(1)	P—C—C ^{a}	120(1)
C—C—C ^{a}	120(1)	C—C—C ^{a}	120(1)

[a] Mean values.

from these solutions by means of slow diffusion of i-propanol yielded black crystals identical to those mentioned above.

This new black compound obtained as the PPN salt dissolves in acetone as readily as the $RuIr_4$ species but has reduced solubility in THF (estimated about 2%). The solutions are brown in color. The IR spectrum is completely different from that of $[RuIr_4(CO)_{15}]^{2-}$ and in THF shows bands at 2025w, 1980vs, 1965s, 1937—1930ms, 1895(sh), 1780m and 1756m cm^{-1}. The shape and position of the bands suggests the presence of both terminal and bridging carbonyls, on a metal framework perhaps no longer consisting of a trigonal bipyramid, and a ratio of metal atoms to negative charge of about three [9,10].

Strikingly, the brown solutions reacted with CO at room temperature and 1 atm pressure, to give back the pentanuclear dianion $[RuIr_4(CO)_{15}]^{2-}$ together with other species, apparently including $[Ir(CO)_4]^-$ [8b,c]. Unfortunately, the black PPN salt proved unsuitable for crystal structure determination.

The structure of $[PPN]_2[RuIr_4(CO)_9(\mu_2\text{-}CO)_6]$ has been determined by single-crystal X-ray diffraction techniques. A view of the anion showing the atom numbering scheme is presented in Fig. 2, while selected bond distances and angles are given in Tables 1 and 2, respectively. The cluster possesses approximate C_s point symmetry, with a mirror plane passing through Ru, Ir(1) and Ir(4) and bisecting the Ir(2)—Ir(3) bond. The trigonal bipyramidal metal framework is elongated with respect to the Ru—Ir(4) direction (vide infra), with average Ir—Ir distances of 3.00 Å involving apical Ir(4) and 2.71 Å in the equatorial plane.

The dianion contains nine terminal CO ligands, with three on each of the apical atoms Ru and Ir(4), and one each on the equatorial Ir(1), Ir(2) and Ir(3). Three bridging carbonyls are found almost in the equatorial plane, a common feature in trigonal bipyramidal species, while two others bridge edges involving Ru and the sixth bridges the Ir(1)—Ir(4) edge. Mean metal—carbon distances for terminal CO groups are as follows: Ru—C 1.86(2) Å, Ir(1—3)—C 1.72(2) Å, Ir(4)—C 1.70(6) Å, while the corresponding mean C—O distance is 1.26(2) Å *. For bridging CO groups mean distances are: Ru—C 2.12(1) Å, Ir—C 1.98(2) Å and C—O 1.32(5) Å.

The PPN cations both take the common bent form [11], with P—N—P angles of 136(2) and 135(2)° and the phenyl groups in a mutually staggered conformation with respect to the P—N—P axes.

Discussion

It is well known that trigonal bipyramidal clusters can occur with 76 or 72 valence electrons [12]. To date, only one example has been reported of a facile interconversion between these two types by means of simple loss of two CO ligands, for the system $[PtRh_4(CO)_{14}]^{2-} \rightarrow [PtRh_4(CO)_{12}]^{2-}$ [7]. In that case a "migration" of the Pt atom from an equatorial to an apical position is observed. Two other 76 e^- species, $[Rh_5(CO)_{15}]^-$ [5] and $[Rh_5(CO)_{14}I]^{2-}$ [4], have been reported to be unstable in N_2 atmosphere, yielding mixtures of anions of completely different nuclearity. The orange $[RuIr_4(CO)_{15}]^{2-}$ is also unstable under N_2, reacting to yield an anionic species that forms brown solutions. The nature of this latter product is still a puzzling question. Further work is in progress, attempting to prepare crystals with a number of cations, in hopes of obtaining material suitable for an X-ray structural determination.

The trigonal bipyramid of $[RuIr_4(CO)_{15}]^{2-}$ is elongated in the direction of the three-fold axis of the metal framework (vide supra), as has been observed for the other 76 e^- species [2—7] and predicted to be the case on the basis of extended-Hückel molecular orbital calculations [12]. To the best of our knowledge, the Ir—Ir distance of 3.038(3) Å between Ir(3) and Ir(4) in the $RuIr_4$ sys-

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* Means are simple unweighted values and e.s.d.'s have been computed as $\sigma(\bar{x}) = \{\Sigma(x_i - \bar{x})^2/n(n-1)\}^{1/2}$.

tem is the longest such bonded distance reported thus far [13]. The Ru—Ir distances are also rather long, falling in the range 2.957(5)—3.046(4) Å with an average value of 3.01 Å. Curiously, here the two longest distances are associated with the edges spanned by the bridging carbonyls CO(25) and CO(35), while for Ir(4) the two longest Ir—Ir distances correspond to non-bridged edges, as is normally the case [9].

Experimental

Synthesis of $[PPN]_2[RuIr_4(CO)_{15}]$

All operations were performed under N_2 or CO as specified. THF was distilled under N_2 from Na/benzophenone; all other analytical grade solvents were used without further purification after degassing in vacuum and storage under N_2. $Ir_4(CO)_{12}$ was prepared and purified by a modification of standard methods [14,15], while $RuCl_3 \cdot x\ H_2O$ and $Ru_3(CO)_{12}$ were obtained commercially. IR spectra were taken routinely with Perkin-Elmer 735 B and 297; for more precise spectra a Beckman IR 7 was employed.

$Ir_4(CO)_{12}$ (0.395 g, 0.357 mmol) and $RuCl_3 \cdot x\ H_2O$ (0.445 g or 1.75 mmol based on a Ru content from atomic absorption analysis of 39.7%, a five-fold excess over $Ir_4(CO)_{12}$) were placed in a Schlenk tube. The system was evacuated and refilled with CO. MeOH (20 ml) and NaOH pellets (0.9 g) subsequently were added. The mixture was stirred vigorously with a magnetic bar and maintained at 1 atm CO pressure by means of a mercury valve. After 24 h a brown-yellow solution was obtained with abundant precipitation, primarily of NaCl and Na_2CO_3. This solution was filtered under CO with a medium sinter, an operation requiring several hours due to the very fine nature of the precipitate. Then [PPN]Cl (2.8 g) in MeOH (8 ml) was added with stirring, resulting in the precipitation of yellow flakes. The product was filtered from the brown-reddish mother liquor under CO, washed with H_2O (4 × 10 ml) and i-propanol * (2 × 10 ml), quickly vacuum dried and stored under CO. Recrystallization was performed under CO by the slow diffusion technique from acetone (6 ml) and i-propanol (30 ml). In about two weeks nicely formed orange crystals were recovered. Yield 0.15 g (18% based on the quantity of $Ir_4(CO)_{12}$ reacted).

Synthesis of the brown anion

$[PPN]_2[RuIr_4(CO)_{15}]$ (0.13 g) was dissolved in THF (5 ml) under N_2; the solution was evacuated and maintained for about 1/2 h in a static vacuum that was renewed occasionally. An IR spectrum taken at this point showed no trace of the original starting material, while the color of the solution had changed to brown. Slow diffusion of i-propanol (10—15 ml) over a few days gave well-shaped black crystals, with a yield of about 0.05 g.

X-ray diffraction studies

A single-crystal sample of $[PPN]_2[RuIr_4(CO)_{15}]$ with approximate dimensions 0.1 × 0.2 × 0.5 mm was mounted in a sealed quartz capillary under N_2. Cell constants were determined based on sin θ values of 25 individually-cen-

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* This latter solvent extracted some brown impurity.

TABLE 3

CRYSTAL DATA AND EXPERIMENTAL DETAILS

Molecular formula	$[((C_6H_5)_3P)_2N]_2[RuIr_4(CO)_{15}]$
Molecular weight	2367.2
Density (calcd.)	1.907 g cm^{-3}
Space group	$P\bar{1}$ ($Z = 2$)
Cell constants:	
$a = 11.425(3)$ Å	$\alpha = 84.55(1)^\circ$
$b = 14.141(2)$ Å	$\beta = 83.53(2)^\circ$
$x = 25.979(5)$ Å	$\gamma = 82.71(2)^\circ$
$V = 4122.9$ Å^3	
Linear absorption coefficient, μ	(Mo-$K_{\bar{\alpha}}$ X-rays) 88.5 cm^{-1}
No. reflections measured	7218
Agreement factor for averaging $R(F^2)$	0.064
No. independent reflections	5766
No. reflections employed in refinement (n)	4481 ($F_0 > 2\sigma(F_0)$)
No. parameters (m)	498
$R(F) = \Sigma \lvert F_0 - k\lvert F_c\rvert\rvert / F_0$	0.083 [a]
$wR(F) = \Sigma(F_0 - k\lvert F_c\rvert)^2/\Sigma F_0{}^2$	0.089 [a]
$S = [\Sigma w(F_0 - k\lvert F_c\rvert)^2/(n - m)]^{1/2}$	1.832 [a]

[a] R and S values are quoted for the 4481 reflections employed in the refinement. For the entire set of 5766 independent reflections. $R(F) = 0.104$ and $wR(F) = 0.116$.

tered reflections widely scattered throughout reciprocal space. No systematic absences were observed and space group $P\bar{1}$ ($Z = 2$) was assumed based on the cell parameters and Laue symmetry. This choice was later confirmed by the structure solution.

Reflections in a full hemisphere out to $2\theta = 40^\circ$ ($\sin \theta/\lambda = 0.48$ Å^{-1}) were samples on an Enraf-Nonius CAD 4 diffractometer with Mo-$K_{\bar{\alpha}}$ radiation ($\lambda = 0.71069$ Å, graphite monochromator). Intensity measurements were performed at room temperature in the $\theta/2\theta$ scan mode. Three monitor reflections were scanned every 3 h. The sample apparently suffered some decomposition, and the data were normalized to allow for approximately 12% decrease in the observed intensities of the monitor reflections over the period of data collection, which lasted about 10 days. Lorentz, polarization, decay and empirical absorption corrections [16] were applied and Friedel pairs and multiple observations were then averaged, yielding $F_0{}^2$ values for 5766 independent reflections, of which 4481 with $F_0 > 2\sigma(F_0)$ were employed in the structure refinement. Experimental quantities of interest are listed in Table 3.

The structure was solved using standard heavy-atom techniques. The model included anisotropic thermal parameters for metal and P atoms and isotropic thermal parameters for the remaining non-hydrogen atoms, comprising a total of 498 variable parameters. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [17] with anomalous dispersion corrections included for Ir, Ru and P. H atoms were not included. All parameters were varied by a block diagonal least-squares procedure minimizing $\Sigma w(F_0 - k\lvert F_c\rvert)^2$, and weights were taken as $w = 1/\sigma^2(F_0)$, where $\sigma^2(F_0) = \sigma^2{}_{count}(F_0{}^2)/(4\,F_0{}^2) + (0.03\,F_0)^2$. Refined atomic coordinates and thermal parameters are listed in Table 4 *. A final difference-Fourier synthesis showed

(continued on p. 377)

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* A listing of structure factors (Table 5) has been deposited with NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017.

TABLE 4

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS [a]

(a) $[\mathrm{RuIr_4(CO)_{15}}]^{2-}$

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir(1)	0.5685(2)	0.3271(1)	−0.30428(7)	0.059(1)	0.054(1)	0.037(1)	−0.008(1)	0.0058(9)	−0.011(1)
Ir(2)	0.5447(2)	0.2106(1)	−0.21478(7)	0.054(1)	0.033(1)	0.047(1)	−0.0005(9)	−0.0080(9)	−0.0032(9)
Ir(3)	0.3915(2)	0.3700(1)	−0.22827(7)	0.042(1)	0.050(1)	0.042(1)	−0.0032(9)	−0.0022(8)	−0.0065(9)
Ir(4)	0.3718(2)	0.2064(2)	−0.29343(9)	0.075(2)	0.049(1)	0.081(2)	−0.016(2)	−0.027(1)	−0.015(1)
Ru	0.6437(3)	0.3988(3)	−0.2114(1)	0.041(2)	0.057(3)	0.054(3)	−0.010(2)	−0.009(2)	−0.006(2)
C(1)	0.666(4)	0.376(4)	−0.349(2)	0.06(1)					
C(2)	0.559(3)	0.092(3)	−0.190(2)	0.04(1)					
C(3)	0.246(4)	0.422(4)	−0.211(2)	0.07(2)					
C(4)	0.426(6)	0.101(5)	−0.310(3)	0.12(2)					
C(5)	0.258(6)	0.269(5)	−0.332(3)	0.12(2)					
C(6)	0.284(6)	0.178(5)	−0.241(3)	0.13(2)					
C(7)	0.703(4)	0.441(4)	−0.156(2)	0.08(2)					
C(8)	0.802(4)	0.355(4)	−0.237(2)	0.07(2)					
C(9)	0.639(4)	0.508(3)	−0.257(2)	0.05(1)					
C(12)	0.666(7)	0.223(6)	−0.278(3)	0.15(3)					
C(13)	0.421(5)	0.425(4)	−0.301(2)	0.09(2)					
C(14)	0.481(3)	0.252(3)	−0.345(1)	0.03(1)					
C(23)	0.396(4)	0.262(4)	−0.170(2)	0.07(2)					
C(25)	0.648(5)	0.261(5)	−0.172(2)	0.10(2)					
C(35)	0.466(4)	0.445(3)	−0.184(2)	0.05(1)					
O(1)	0.747(3)	0.409(3)	−0.377(2)	0.10(1)					
O(2)	0.563(3)	0.001(3)	−0.172(1)	0.09(1)					
O(3)	0.136(3)	0.462(3)	−0.203(2)	0.11(1)					
O(4)	0.477(4)	0.012(4)	−0.321(2)	0.13(2)					
O(5)	0.175(5)	0.312(4)	−0.349(2)	0.17(2)					
O(6)	0.228(4)	0.137(3)	−0.199(2)	0.12(2)					
O(7)	0.734(3)	0.471(3)	−0.119(1)	0.09(1)					
O(8)	0.890(4)	0.323(3)	−0.260(2)	0.13(2)					
O(9)	0.639(3)	0.588(3)	−0.280(1)	0.08(1)					
O(12)	0.736(3)	0.130(2)	−0.298(1)	0.07(1)					
O(13)	0.386(3)	0.499(2)	−0.333(1)	0.067(9)					
O(14)	0.514(3)	0.255(3)	−0.396(1)	0.10(1)					
O(23)	0.350(3)	0.250(3)	−0.123(1)	0.09(1)					
O(25)	0.697(3)	0.226(2)	−0.136(1)	0.08(1)					
O(35)	0.425(3)	0.512(3)	−0.159(2)	0.11(1)					

P(11)	0.1520(9)	−0.1879(8)	−0.1313(4)	0.039(7)	0.030(7)	0.031(6)	0.001(5)	−0.017(5)	0.002(5)
P(12)	0.2571(9)	−0.1702(8)	−0.0344(4)	0.028(6)	0.043(8)	0.030(6)	0.000(5)	−0.009(5)	−0.009(6)
N(1)	0.230(3)	−0.145(2)	−0.091(1)	0.048(9)					
C(1A)	0.045(3)	−0.086(2)	−0.152(1)	0.012(8)					
C(2A)	0.047(3)	−0.001(3)	−0.132(2)	0.05(1)					
C(3A)	−0.042(3)	0.074(3)	−0.154(1)	0.04(1)					
C(4A)	−0.112(4)	0.062(3)	−0.188(2)	0.04(1)					
C(5A)	−0.108(3)	−0.032(3)	−0.206(1)	0.04(1)					
C(6A)	−0.031(4)	−0.109(3)	−0.187(2)	0.05(1)					
C(1B)	0.245(4)	−0.224(3)	−0.190(2)	0.05(1)					
C(2B)	0.340(4)	−0.172(4)	−0.206(2)	0.07(2)					
C(3B)	0.395(5)	−0.205(4)	−0.256(2)	0.09(2)					
C(4B)	0.375(4)	−0.271(4)	−0.279(2)	0.07(1)					
C(5B)	0.279(4)	−0.318(4)	−0.262(2)	0.07(1)					
C(6B)	0.210(3)	−0.300(3)	−0.214(2)	0.05(1)					
C(1C)	0.073(4)	−0.289(3)	−0.104(2)	0.05(1)					
C(2C)	0.138(4)	−0.386(3)	−0.098(2)	0.06(1)					
C(3C)	0.061(5)	−0.460(4)	−0.073(2)	0.09(2)					
C(4C)	−0.047(5)	−0.431(4)	−0.059(2)	0.08(2)					
C(5C)	−0.110(4)	−0.340(4)	−0.057(2)	0.07(2)					
C(6C)	−0.047(4)	−0.268(3)	−0.086(2)	0.05(1)					
C(1D)	0.383(3)	−0.260(2)	−0.027(1)	0.022(9)					
C(2D)	0.429(3)	−0.311(3)	−0.069(2)	0.04(1)					
C(3D)	0.516(4)	−0.383(3)	−0.063(2)	0.06(1)					
C(4D)	0.574(4)	−0.397(4)	−0.017(2)	0.07(1)					
C(5D)	0.528(3)	−0.343(3)	0.028(1)	0.04(1)					
C(6D)	0.428(3)	−0.277(3)	0.019(1)	0.03(1)					
C(1E)	0.131(3)	−0.206(3)	0.011(1)	0.03(1)					
C(2E)	0.148(3)	−0.295(3)	0.042(1)	0.04(1)					
C(3E)	0.039(4)	−0.314(3)	0.075(2)	0.06(1)					
C(4E)	−0.066(4)	−0.243(4)	0.073(2)	0.08(2)					
C(5E)	−0.082(4)	−0.177(3)	0.039(2)	0.05(1)					
C(6E)	0.024(4)	−0.145(3)	0.008(2)	0.05(1)					
C(1F)	0.293(3)	−0.063(3)	−0.013(2)	0.04(1)					
C(2F)	0.271(4)	−0.044(3)	0.041(2)	0.06(1)					
C(3F)	0.303(4)	0.043(3)	0.053(2)	0.06(1)					
C(4F)	0.362(4)	0.103(3)	0.018(2)	0.06(1)					
C(5F)	0.386(3)	0.084(3)	−0.029(2)	0.04(1)					
C(6F)	0.354(3)	0.001(3)	−0.047(1)	0.03(1)					
P(21)	0.0878(9)	0.2060(8)	0.3533(5)	0.034(7)	0.039(8)	0.062(8)	−0.018(6)	−0.010(6)	−0.011(6)
P(22)	0.2088(9)	0.1809(8)	0.4481(4)	0.032(7)	0.035(7)	0.038(7)	−0.004(5)	−0.006(5)	−0.009(6)
N(2)	0.192(3)	0.174(2)	0.388(1)	0.034(8)					
C(1G)	−0.016(3)	0.302(3)	0.376(2)	0.05(1)					
C(2G)	−0.130(4)	0.294(4)	0.398(2)	0.08(2)					
C(3G)	−0.210(5)	0.371(4)	0.416(2)	0.10(2)					

TABLE 4 (continued)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(4G)	−0.163(5)	0.460(5)	0.411(2)	0.10(2)					
C(5G)	−0.052(5)	0.473(5)	0.394(2)	0.11(2)					
C(6G)	0.029(5)	0.392(4)	0.373(2)	0.08(2)					
C(1H)	0.150(4)	0.247(3)	0.291(2)	0.05(1)					
C(2H)	0.098(4)	0.310(4)	0.258(2)	0.07(1)					
C(3H)	0.135(5)	0.339(4)	0.212(2)	0.08(2)					
C(4H)	0.238(4)	0.298(3)	0.190(2)	0.06(1)					
C(5H)	0.304(5)	0.221(4)	0.216(2)	0.08(2)					
C(6H)	0.256(5)	0.193(4)	0.273(2)	0.08(2)					
C(1I)	0.010(3)	0.106(3)	0.346(1)	0.03(1)					
C(2I)	−0.091(4)	0.122(4)	0.315(22)	0.07(1)					
C(3I)	−0.151(5)	0.045(4)	0.309(2)	0.08(2)					
C(4I)	−0.107(3)	−0.048(3)	0.328(1)	0.04(1)					
C(5I)	−0.006(4)	−0.060(4)	0.355(2)	0.07(1)					
C(6I)	0.055(4)	0.015(3)	0.363(2)	0.05(1)					
C(1J)	0.277(3)	0.068(3)	0.476(1)	0.03(1)					
C(2J)	0.347(4)	0.010(3)	0.443(2)	0.06(1)					
C(3J)	0.408(4)	−0.072(4)	0.468(2)	0.07(1)					
C(4J)	0.392(5)	−0.096(4)	0.518(2)	0.08(2)					
C(5J)	0.321(4)	−0.038(4)	0.553(2)	0.07(2)					
C(6J)	0.260(4)	0.041(3)	0.531(2)	0.05(1)					
C(1K)	0.070(3)	0.209(3)	0.487(2)	0.04(1)					
C(2K)	−0.004(4)	0.138(3)	0.495(2)	0.05(1)					
C(3K)	−0.122(4)	0.161(4)	0.520(2)	0.06(1)					
C(4K)	−0.148(5)	0.240(4)	0.546(2)	0.09(2)					
C(5K)	−0.068(6)	0.323(6)	0.536(3)	0.15(3)					
C(6K)	0.034(4)	0.301(3)	0.509(2)	0.05(1)					
C(1L)	0.301(3)	0.275(3)	0.453(1)	0.03(1)					
C(2L)	0.337(4)	0.292(3)	0.503(2)	0.05(1)					
C(3L)	0.417(4)	0.359(3)	0.507(2)	0.06(1)					
C(4L)	0.455(4)	0.411(4)	0.453(2)	0.08(2)					
C(5L)	0.429(4)	0.384(3)	0.404(2)	0.06(1)					
C(6L)	0.346(4)	0.320(3)	0.406(2)	0.06(1)					

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[a] Thermal parameters are of the form $\exp\{-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})\}$. For C, N and O atoms, which were refined isotropically, only U_{11} is given.

several ghost peaks, presumably due to series-termination effects, lying in a range within 1.5 Å of the metal atoms, but no significant peaks were found that could sensibly be assigned as H atoms.

Crystals of the black PPN salt unfortunately gave very poor quality diffraction patterns and a structure solution has thus far not been possible. However, a triclinic cell was determined with $a = 12.44(7)$, $b = 14.08(5)$, $c = 14.16(4)$ Å, $\alpha = 60.5(3)$, $\beta = 89.3(4)$, $\gamma = 88.8(4)^\circ$, and $V = 2158$ Å^3. Based on an observed density of 1.945 g cm^{-3} obtained by flotation with two different crystals, and assuming $Z = 1$, the molecular weight is estimated at 2530. Intensities of selected reflections with $\sin \theta/\lambda < 0.24$ Å^{-1} were measured and a Patterson synthesis showed evidence for at least five metal atoms, all refined at present as Ir, arranged as a distorted tetrahedron with one bridged edge and $R(F) = 0.23$. A complete analytical determination could not be obtained due to the very small samples, but atomic absorption measurements confirmed the presence of both Ru and Ir.

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