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Synthesis and structural characterization of the mixed-metal species $[Co_2Ir_2(CO)_{10}(\eta^4\text{-cod})]$ and $[CoIr_3(CO)_{10}(\eta^4\text{-cod})]$ (cod = 1,5-cyclooctadiene)

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Abstract

The new mixed-metal clusters $[Co_2Ir_2(CO)_{10}(cod)]$ (**4**) and $[CoIr_3(CO)_{10}(cod)]$ (**5**) (cod = 1,5-cyclooctadiene) have been obtained from $[Co_2(CO)_8]$ (**2**) and $[\{IrCl(cod)\}_2]$ (**3**). Alternatively, $[Co_2Ir_2(CO)_{12}]$ (**1**) reacts with cod to yield **4**, which in the presence of CO reforms **1**. Under the same conditions, however, **5** is inert. The solid state structures of **4** and **5** have been established by X-ray analyses, and the disorder shown by the two species is discussed. Compound **4** is monoclinic, space group $P2_1/c$, a 8.891(2), b 10.746(3), c 22.648(8) Å, β 95.16(3)°, $Z = 4$, $R = 0.048$, $R' = 0.050$, for 2393 $[I > 2\sigma(I)]$ of 2596 absorption corrected reflections; compound **5** is also monoclinic, space group $P2_1/m$, a 8.5994(9), b 12.047(3), c 10.799(3) Å, β 98.30(1)°, $Z = 2$, $R = 0.037$, $R' = 0.040$, for 2071 $[I > 2\sigma(I)]$ of 2711 absorption corrected reflections.

1. Introduction

The substitution reactions of $[Ir_4(CO)_{12}]$ with cod (cod = 1,5-cyclooctadiene) have been the subject of previous studies. Species containing as many as three cod ligands, *i.e.* $[Ir_4(CO)_{12-2x}(cod)_x]$ ($x = 1$–3) have been isolated from the reaction of the binary carbonyl with cod in the presence of Me_3NO [1]. A high-yield synthesis of $[Ir_4(CO)_{10}(cod)]$ has also been discovered, starting from $[Ir_4(CO)_{11}Br]^-$ [2,3]. In the case of $[Co_4(CO)_{12}]$, however, attempted substitution of CO by diolefins was found to be complicated by changes in the nuclearity of the cluster [4]. We became interested in studying the CO substitution-chemistry of the mixed-metal cluster analogue $[Co_2Ir_2(CO)_{12}]$ (**1**) [5], both with diolefins and phosphines; only one report on the reactions of this species with $P(OMe)_3$ has appeared in the literature [6], although $[Co_2Ir_2(CO)_8(PF_3)_4]$ has been synthesised from the reaction of $[\{IrCl(PF_3)_2\}_2]$ and $Tl[Co(CO)_4]$ [7]. Besides possible site selectivity, a higher thermal stability due to the presence of Ir–Ir bonds was expected, compared to the Co_4 system. We report here that a modification of the synthetic route to $[Co_2Ir_2(CO)_{12}]$ [6] that uses $[Co_2(CO)_8]$ (**2**) and $[\{IrCl(cod)\}_2]$ (**3**) as starting materials yields $[Co_2Ir_2(CO)_{12-x}(cod)_x]$ [$x = 1$ (**4**) or 2 (**6**)] and $[CoIr_3(CO)_{12-x}(cod)_x]$ [$x = 1$ (**5**) or 2 (**7**)].

2. Results and discussion

2.1. *Synthesis and chemical characterization*

The mixed-metal cluster $[Co_2Ir_2(CO)_{12}]$ (**1**) was first synthesised from the reaction of $Na[Co(CO)_4]$ and $K_2[Ir(CO)I_5]$ in 60–70% yield [5]. A later route to this species used $[Co_2(CO)_8]$ (**2**) and $[\{IrCl(cod)\}_2]$ (**3**) as starting materials [6] but no preparative details were given and we were unable to produce **1** in the claimed 60% yield. Investigations of this reaction under a variety of conditions has shown that best yields of **1** are obtained when a hexane solution of **2** and **3** in 3/2 molar ratio is stirred for 24 h at room temperature, and

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the resulting solid filtered and washed with a little CH_2Cl_2, instead of hexane as reported, before the solution finally obtained is cooled for crystallization.

When the molar ratio of **2**/**3** is 0.5, four other products are obtained, which run on the TLC plates very closely together in pairs: the brown species $[Co_2Ir_2(CO)_{10}(cod)]$ (**4**) and the red compound $[CoIr_3(CO)_{10}(cod)]$ (**5**), in about 25% yield each, as well as the tetrasubstituted red and green species, $[Co_2Ir_2(CO)_8(cod)_2]$ (**6**) and $[CoIr_3(CO)_8(cod)_2]$ (**7**), in yields less than 5%. A dark residue is invariably left on the TLC plates. Compounds **4** and **5** have very similar IR solution spectra in the ν(CO) region, with three bands characteristic of bridging CO, as shown in Fig. 1. Their room temperature ^{1}H NMR spectra show in both cases three distinct multiplets due to the cyclooctadiene [**4**: δ 3.68, 2.88, and 2.06; **5**: δ 3.58, 2.77, and 2.02 ppm]. This is comparable to that reported for $[Ir_4(CO)_{10}(cod)]$ at the coalescence temperature, with multiplets [δ 3.98, 2.78 and 2.00] corresponding to the axial and radial olefinic protons, the outer CH_2, and the inner CH_2 protons, respectively [3].

Compounds **4** and **5** were initially thought to be two isomers of **4**. However, when these species are heated in toluene at 50°C for 1 h under slightly more than one atmosphere of CO, only compound **4** is converted quantitatively to the binary carbonyl **1**, whereas compound **5** is still inert. At 60°C it starts to decompose. The FAB-MS of these compounds was not useful in establishing their identity. Even though redistribution was not noted in the MS spectrum of **1** (compare the spectra of other mixed-metal clusters of this series, *e.g.* $Co_2Rh_2(CO)_{12}$ and $Rh_2Ir_2(CO)_{12}$ [5]) we were not able to identify unequivocally M^+ peaks in the spectra of **4** and **5**. Elemental analyses established their identity, and in order to determine unambiguously their molecular structures X-ray analyses of both species were undertaken. Compounds **6** and **7** have only been characterized by IR spectroscopy. As shown in Fig. 2, their IR spectra are extremely similar, with all ν(CO) frequencies shifted by about 25 cm^{-1} when compared to the spectra of the disubstituted compounds **4** and **5**, a consequence of CO substitution by ligands donating more than two electrons [3].

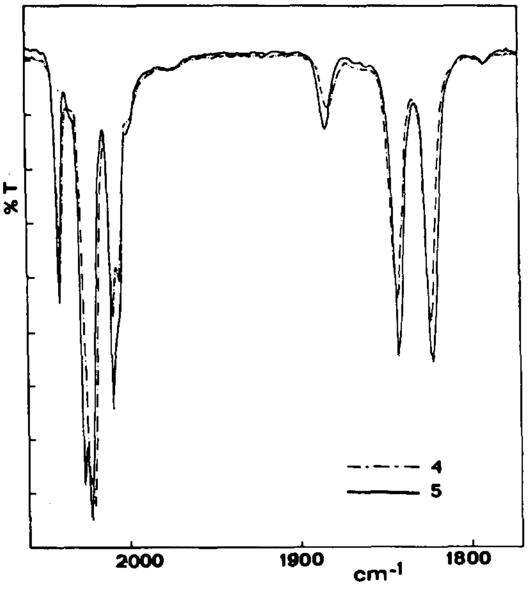

Fig. 1. IR spectra of compounds **4** and **5** in hexane.

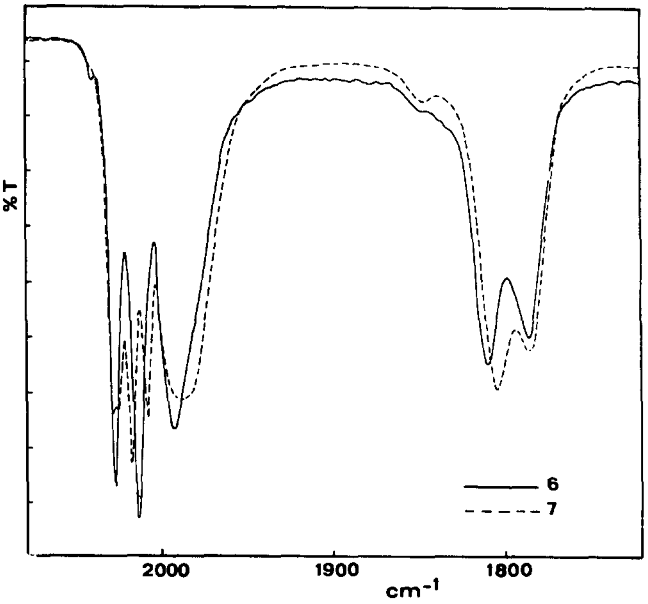

Fig. 2. IR spectra of compounds **6** and **7** in hexane.

2.2. *Structural characterization in the solid state*

The molecular structures of **4** and **5** in the solid state (see Figs. 3 and 4) are closely related. Relevant structural parameters are listed in Tables 1 and 2.

Both cluster frameworks are based on the familiar tetrahedron of metal atoms common to most $[M_4(CO)_{12}]$ derivatives [M = Co, Rh, or Ir] [8]. In **4** the two Co atoms form an edge of the tetrahedron base bearing the bridging CO ligands and the terminally bound cod (see Fig. 3). A similar situation is found in **5**, where the bridged basal triangle (see Fig. 4) contains the single Co atom.

There is a certain degree of positional disorder in **4**, involving one of the Co atoms [Co(1)] and the apical Ir atom. The best disorder model was obtained with the Co/Ir occupancy ratio of 4/5 and 1/5 for the basal and apical atoms, respectively. The same kind of disorder involving the tetrahedron of metal atoms was observed in [$Co_2Ir_2(CO)_{12}$] (**1**) [5b]. As expected on the basis of the synthetic method, in both **4** and **5** the cod is coordinated to an Ir atom, formally replacing an axial and a radial terminal CO. Metal–metal bond lengths reflect the complex system of heteroatomic bonding present in the two clusters.

The structural analysis of **5** is complicated by the presence of ligand disorder. The molecule contains a crystallographic mirror plane, which comprises Ir(1), the Co atom and two of the C(cod) atoms, and passes through the midpoint of the Ir(2)–Ir(2′) bond. This symmetry element relates the points at which the CO and cod are disordered.

Of the three pure Ir–Ir bonds both Ir(1)–Ir(2) and its symmetry related Ir(1)–Ir(2′) are bridged by CO (but only the former is shown as bridged in Fig. 4), and are longer than the unbridged Ir(2)–Ir(2′) bond [2.710(1) and 2.695(1) Å, respectively]. This is in keeping with our previous observation that CO-bridging on Ir–Ir bonds does not shorten the metal–metal separations [9].

The M–C(CO) bond lengths also show a marked dependence on the metal atom radius. This is particularly appreciable within the bridging CO systems, which tend to be asymmetric as expected with longer distances from the Ir atoms (see Table 1). As mentioned above, in both **4** and **5** the chelating cod occupies a basal site and adopts a boat conformation. Ir–C(cod) distances in **4** do not show appreciable differences, whether radial or axial. However, the presence of disorder in **5** prevents a more detailed comparison of the structural parameters of the light atoms in the two species. The same mode of coordination for the diolefin has been found in other cod derivatives such as [$Ir_4(CO)_{10}$(cod)] [10] and [$Ir_4(CO)_5$(cod)(C_8H_{10})] [1] and in the phosphine clusters [$Ir_4(CO)_9PPh_3$(nbd)] [11] (nbd = 2,3-η : 5,6-η-norbornadiene), and [$Ir_4(CO)_9$-PMe_2Ph(nbd)] [11].

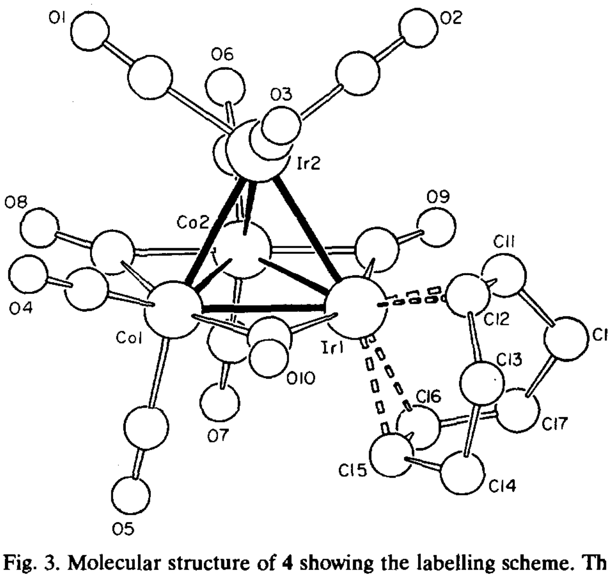

Fig. 3. Molecular structure of **4** showing the labelling scheme. The C atoms of the CO groups bear the same numbering as the corresponding O atoms.

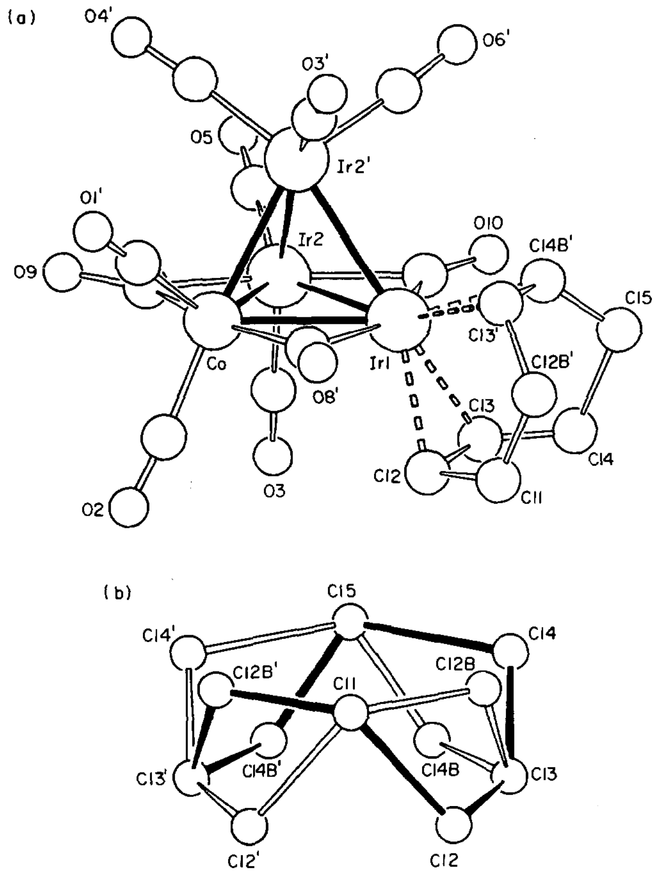

Fig. 4. (a) Molecular structure of **5** showing the labelling scheme. The C atoms of the CO groups bear the same numbering as the corresponding O atoms. The crystallographic mirror plane bisects the Ir(2)–Ir(2′) bond and contains Co, Ir1, C11 and C15; primed atoms are symmetry-related (note that only the pairs C3O3/C3′O3′ and C13/C13′ belong to the same disorder image). For the sake of clarity the disorder model affecting the cod ligand is shown in (b).

3. Experimental details

3.1. Material and methods

All manipulations and reactions were performed under an atmosphere of dry argon, unless otherwise specified, by using Schlenk-type glassware. All solvents were treated with the appropriate drying agent and distilled under argon before use. The progress of the reactions was monitored by analytical TLC (0.25 mm thick, glass-backed silica gel plates prepared from silica Gel GF 254 Type 60, Fluka) and IR spectra, recorded on a JASCO IR 700 instrument between 2200 and 1600 cm^{-1} using CaF_2 cells. Preparative TLC was carried out in air using *ca.* 2-mm thick glass-backed silica gel plates (20 × 20 cm) prepared as above. ^1H NMR data were obtained on a Bruker AC 300/P instrument. Fast atom bombardment mass spectra (FAB-MS) were obtained on a Kratos MS50, the atom being produced by an Ion Tech FAB gun, operating with xenon at 8 kV with a current of 40 μA and using *p*-nitrobenzyl alcohol as a matrix, at the University Chemical Laboratory, University of Cambridge, UK.

The compounds $[\{IrCl(cod)\}_2]$ [12] and $[Co_2Ir_2(CO)_{12}]$ [6] were prepared by published procedures, the latter with the modifications described below; all other reagents were purchased from commercial sources and used as supplied.

TABLE 1. Relevant bond distances (Å) and angles (°) for **4**

Co(1)–Co(2)	2.496(3)	C(1)–O(1)	1.13(3)
Co(1)–Ir(1)	2.624(2)	C(2)–O(2)	1.13(2)
Co(1)–Ir(2)	2.612(2)	C(3)–O(3)	1.14(3)
Co(2)–Ir(1)	2.636(2)	C(4)–O(4)	1.16(3)
Co(2)–Ir(2)	2.578(2)	C(5)–O(5)	1.07(2)
Ir(1)–Ir(2)	2.683(1)	C(6)–O(6)	1.14(3)
		C(7)–O(7)	1.14(2)
Ir(2)–C(1)	1.90(2)	C(8)–O(8)	1.17(2)
Ir(2)–C(2)	1.91(2)	C(9)–O(9)	1.17(2)
Ir(2)–C(3)	1.86(2)	C(10)–O(10)	1.19(2)
Co(1)–C(4)	1.75(3)		
Co(1)–C(5)	1.85(2)	Ir(1)–C(11)	2.21(2)
Co(2)–C(6)	1.73(2)	Ir(1)–C(12)	2.21(2)
Co(2)–C(7)	1.81(2)	Ir(1)–C(15)	2.23(2)
Co(1)–C(8)	1.93(2)	Ir(1)–C(16)	2.22(2)
Co(2)–C(8)	1.95(2)		
Co(2)–C(9)	1.95(2)	C(11)–C(12)	1.41(3)
Ir(1)–C(9)	2.07(2)	C(11)–C(18)	1.46(3)
Co(1)–C(10)	1.96(2)	C(12)–C(13)	1.51(3)
Ir(1)–C(10)	2.04(2)	C(13)–C(14)	1.61(3)
		C(14)–C(15)	1.54(3)
O(1)–C(1)–Ir(2)	178(2)	C(15)–C(16)	1.38(3)
O(2)–C(2)–Ir(2)	178(2)	C(16)–C(17)	1.49(3)
O(3)–C(3)–Ir(2)	176(2)	C(17)–C(18)	1.55(3)
O(4)–C(4)–Co(1)	180(2)		
O(5)–C(5)–Co(1)	180(2)		
O(6)–C(6)–Co(2)	172(2)		
O(7)–C(7)–Co(2)	175(2)		
O(8)–C(8)–Co(1)	141(2)		
O(8)–C(8)–Co(2)	139(2)		
O(9)–C(9)–Cr(2)	137(2)		
O(9)–C(9)–Ir(1)	141(2)		
O(10)–C(10)–Co(1)	134(2)		
O(10)–C(10)–Ir(1)	144(2)		

TABLE 2. Relevant bond distances (Å) and angles (°) for **5**

Co–Ir(1)	2.669(2)	C(1)–O(1)	1.06(4)
Co–Ir(2)	2.606(1)	C(2)–O(2)	1.12(4)
Ir(1)–Ir(2)	2.710(1)	C(3)–O(3)	1.12(2)
Ir(2)–Ir(2)	2.695(1)	C(4)–O(4)	1.13(4)
		C(5)–O(5)	1.08(4)
Co–C(1)	1.82(3)	C(6)–O(6)	1.14(4)
Co–C(2)	1.79(3)	C(8)–O(8)	1.17(4)
Ir(2)–C(3)	1.91(2)	C(9)–O(9)	1.26(3)
Ir(2)–C(4)	1.91(3)	O(10)–C(10)	1.22(3)
Ir(2)–C(5)	1.88(2)		
Ir(2)–C(6)	1.91(3)	Ir(1)–C(13)	2.21(1)
Co–C(8)	1.92(3)	Ir(1)–C(12)	2.23(3)
Ir(1)–C(8)	2.11(3)	Ir(1)–C(14B)	2.16(3)
Co–C(9)	1.87(2)		
Ir(2)–C(9)	2.07(2)	C(11)–C(12)	1.61(5)
Ir(1)–C(10)	2.07(2)	C(11)–C(12B)	1.48(3)
Ir(2)–C(10)	2.08(2)	C(12)–C(13)	1.47(3)
		C(12B)–C(13)	1.53(4)
O(1)–C(1)–Co	177(3)	C(13)–C(14)	1.38(3)
O(2)–C(2)–Co	176(3)	C(13)–C(14B)	1.47(3)
O(3)–C(3)–Ir(2)	178(1)	C(14)–C(15)	1.77(4)
O(4)–C(4)–Ir(2)	176(3)	C(14B)–C(15)	1.43(3)
O(5)–C(5)–Ir(2)	176(3)		
O(6)–C(6)–Ir(2)	176(3)		
O(8)–C(8)–Co	142(2)		
O(8)–C(8)–Ir(1)	135(2)		
O(9)–C(9)–Co	141(2)		
O(9)–C(9)–Ir(2)	136(2)		
O(10)–C(10)–Ir(1)	142(2)		
O(10)–C(10)–Ir(2)	137(2)		

3.2. *Preparation of 1*

A suspension of $[Co_2(CO)_8]$ (296 mg, 0.867 mmol) and $[\{IrCl(cod)\}_2]$ (388 mg, 0.578 mmol) in hexane (20 ml) was stirred for 24 h at room temperature. The mixture was filtered, the solid washed with CH_2Cl_2 (2 × 10 ml), and the solvent mixture evaporated. The dark product was purified by TLC with CH_2Cl_2/hexane (1/4) as eluent, affording $[Co_2Ir_2(CO)_{12}]$ (**1**) (300 mg, 63%) and decomposition products.

3.3. *Preparation of the cod-substituted species 4, 5, 6 and 7*

A suspension of $[Co_2(CO)_8]$ (**2**) (23 mg, 0.067 mmol) and $[\{IrCl(cod)\}_2]$ (**3**) (91 mg, 0.13 mmol) in hexane (10 cm^3) was stirred for 24 h at 25°C. The mixture was filtered, washed with CH_2Cl_2 and the solvent evaporated. The dark product mixture was separated by TLC, and after several consecutive separations with CH_2Cl_2/hexane (1/4), four products were obtained, and crystallized from hexane solutions at −15°C: $[Co_2Ir_2(CO)_{10}(cod)]$ (**4**), brown, (15 mg, 25%), (Found:

C, 24.0; H, 1.2; $C_{18}H_{12}Co_2Ir_2O_{10}$ calc.: C, 24.3; H, 1.4%); ν(CO) (cm^{-1}): 2084m, 2050vs, 2044vs, 2022m, 2014m, 1886vw, 1847m, 1827m (hexane); δ(H) ($CDCl_3$) 3.68 (br, 2CH); 2.88 (br, 2CH); 2.06 (br, $4CH_2$) ppm; $[CoIr_3(CO)_{10}(cod)]$ (**5**), red, (17 mg, 25%) (Found: C, 23.3; H, 1.5; $C_{18}H_{12}CoIr_3O_{10} \cdot 1/2C_6H_{14}$ calc.: C, 23.6; H, 1.8%); ν(CO) (cm^{-1}): 2084m, 2056vs, 2048vs, 2022s, 2016m(sh), 1888vw, 1846m, 1826m (hexane); δ(H) ($CDCl_3$) 3.58 (br, 2CH); 2.77 (br, 2CH); 2.00 (br, $4CH_2$) ppm; $[Co_2Ir_2(CO)_8(cod)_2]$ (**6**) green, (3.1 mg, 5%); ν(CO) (cm^{-1}): 2082vw, 2060s, 2032vs, 1999s, 1987m, 1821s, 1794s (hexane), and $[CoIr_3(CO)_8(cod)_2]$ (**7**), green, (3.5 mg, 5%); ν(CO) (cm^{-1}): 2062m, 2054vs, 2040vs, 1998s, 1818m, 1805w, 1793m, 1781w (hexane).

3.4. Reactions of 4 and 5 with CO

A solution of **4** (10 mg, 0.011 mmol) in toluene (5 cm^3) was stirred and heated at 50°C for 1 h under slightly more than 1 atm CO. The reaction yielded only $[Co_2Ir_2(CO)_{12}]$ (**1**) (8.9 mg, 95%). Under the same reaction conditions no reaction was observed for **5**, and above 60°C decomposition of **5** was observed.

3.5. Reaction of 1 with cod

A suspension of $[Co_2Ir_2(CO)_{12}]$ (**1**) (30 mg, 0.036 mmol) in THF (10 cm^3) and cod (4.5 μl, 0.043 mmol) was heated under reflux in toluene for 1 h, after which time the solvent was evaporated, the mixture separated by TLC (CH_2Cl_2/hexane 15%) affording **4** (16 mg, 50%), unreacted **1** and decomposition products.

3.6. Crystal structure determination

Crystal data and details of measurements for both **4** and **5** are reported in Table 3. Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer. The structures were solved by

TABLE 3. Crystal data and details of measurements for **4** and **5**

	4		**5**
Formula	$C_{18}H_{12}Co_2Ir_2O_{10}$		$C_{18}H_{12}CoIr_3O_{10}$
M_r	890.6		1023.8
Crystal size (mm)	0.13 × 0.15 × 0.12		0.10 × 0.15 × 0.14
System		monoclinic	
Space group	$P2_1/c$		$P2_1/m$
a (Å)	8.891(2)		8.5994(9)
b (Å)	10.746(3)		12.047(3)
c (Å)	22.648(8)		10.799(3)
β (°)	95.16(3)		98.30(1)
U (Å³)	2155.1		1107.0
Z	4		2
$F(000)$	1632		916
D_{calcd} ($g\ cm^{-3}$)	2.74		3.07
(Mo Kα) (Å)		0.71069	
μ(Mo Kα) (cm^{-1})	133.70		180.82
θ range (°)	2.5–25		2.5–28
Scan mode		$\omega/2\theta$	
ω-scan width (°)	1.70		0.90
Requested counting $\sigma(I)/I$		0.02	
Prescan rate (deg min^{-1})		5	
Prescan acceptance $\sigma(I)/I$		0.5	
Maximum scan time (s)	90		100
Measured reflections	2576		2711
Unique observed reflections used in the refinement $[I > 2\sigma(I)]$ (n)	2393		2071
No. of refined parameters (m)	291		241
Absorption correction (min. and max. correction factors)	0.78–1.00		0.77–1.00
R, R' [a]	0.048, 0.050		0.037, 0.040
S [b]	1.32		1.36
k, g	0.65, 0.0051		1.09, 0.0010

[a] $R' = \Sigma[(F_o - F_c)w^{1/2}]/\Sigma F_o w^{1/2})$, where $w = k/[\sigma^2(F) + |g|F^2]$. [b] $S = \Sigma[(F_o - F_c)/\sigma]^2/(n - m)$.

direct methods, which were used to locate the positions of Co and Ir atoms, followed by difference Fourier syntheses. Both structural models were refined by means of full-matrix least-squares. The structure of **5** was first solved in the non-centric space group $P2_1$ and subsequently refined in the correct space group $P2_1/m$. For all calculations the SHELX76 program was used [13]. Absorption corrections were applied by azimuthal scanning of 6 reflections ($\theta > 80°$) in **4**, and by the Walker and Stuart method [14] in **5**, once a complete structural model was obtained and all atoms refined isotropically. Hydrogen atoms were added in calculated positions in **4** (C–H 1.08 Å) and refined "riding" on their corresponding C atoms. The disorder affecting the cod ligand prevented us from attributing reasonable positions to the H atoms in **5**. All atoms except the H atoms were allowed to vibrate anisotropically in both **4** and **5**. Two single isotropic parameters were refined for the H(CH) and $H(CH_2)$ atoms in **4** [0.08(4) and 0.11(4) Å^2, respectively]. Fractional coordinates for **4** and **5** are listed in Tables 4 and 5, respectively.

TABLE 4. Fractional atomic coordinates for 4

Atom	x	y	z
Co(1)	0.6839(2)	0.3696(2)	0.6034(1)
Co(2)	0.9238(2)	0.2935(2)	0.5667(1)
Ir(1)	0.75994(7)	0.13641(6)	0.62328(3)
Ir(2)	0.91554(8)	0.32224(7)	0.67935(3)
C(1)	0.9988(26)	0.4856(22)	0.6812(7)
O(1)	1.0532(23)	0.5808(15)	0.6826(7)
C(2)	1.0848(20)	0.2207(20)	0.7060(8)
O(2)	1.1824(18)	0.1592(19)	0.7226(9)
C(3)	0.8136(25)	0.3194(16)	0.7474(10)
O(3)	0.7585(20)	0.3185(18)	0.7909(7)
C(4)	0.6046(26)	0.4960(25)	0.6384(11)
O(4)	0.5533(24)	0.5800(19)	0.6615(9)
C(5)	0.5613(23)	0.3557(18)	0.5333(10)
O(5)	0.4896(17)	0.3480(16)	0.4929(7)
C(6)	1.1133(23)	0.3320(22)	0.5693(9)
O(6)	1.2342(20)	0.3681(22)	0.5753(9)
C(7)	0.8805(21)	0.2667(20)	0.4883(9)
O(7)	0.8433(18)	0.2530(18)	0.4394(7)
C(8)	0.8380(23)	0.4608(19)	0.5673(8)
O(8)	0.8691(16)	0.5622(13)	0.5542(6)
C(9)	0.9653(23)	0.1204(18)	0.5873(9)
O(9)	1.0613(19)	0.0485(16)	0.5812(8)
C(10)	0.5889(18)	0.2431(17)	0.6500(9)
O(10)	0.4864(16)	0.2436(14)	0.6803(7)
C(11)	0.8340(21)	−0.0411(17)	0.6656(9)
C(12)	0.7118(21)	0.0051(18)	0.6944(8)
C(13)	0.5514(27)	−0.0432(23)	0.6870(11)
C(14)	0.4894(25)	−0.0575(26)	0.6185(11)
C(15)	0.5645(23)	0.0342(21)	0.5779(10)
C(16)	0.6924(25)	0.0035(20)	0.5508(10)
C(17)	0.7694(31)	−0.1186(23)	0.5605(12)
C(18)	0.8172(32)	−0.1490(21)	0.6263(10)

TABLE 5. Fractional atomic coordinates for 5

Atom	x	y	z
Co	0.90813(19)	0.25000	0.84888(16)
Ir(1)	0.76281(6)	0.25000	0.61312(5)
Ir(2)	0.64739(5)	0.13816(4)	0.79767(4)
C(1)	0.9738(32)	0.1364(21)	0.9541(27)
O(1)	1.0175(35)	0.0722(22)	1.0171(29)
C(2)	1.0816(30)	0.1656(21)	0.8717(26)
O(2)	1.1937(27)	0.1174(24)	0.8921(39)
C(3)	0.7150(18)	−0.0105(13)	0.7741(15)
O(3)	0.7504(18)	−0.0976(10)	0.7570(16)
C(4)	0.5845(42)	0.1258(23)	0.9599(27)
O(4)	0.5563(32)	0.1215(20)	1.0584(21)
C(5)	0.4652(23)	0.1103(20)	0.8708(25)
O(5)	0.3619(30)	0.1006(22)	0.9153(29)
C(6)	0.4465(36)	0.1263(24)	0.6966(28)
O(6)	0.3246(25)	0.1151(23)	0.6412(28)
C(8)	0.9697(32)	0.1754(23)	0.7064(25)
O(8)	1.0597(28)	0.1101(20)	0.6795(26)
C(9)	0.8035(24)	0.1681(20)	0.9589(21)
O(9)	0.8120(30)	0.1431(20)	1.0732(17)
C(10)	0.5569(25)	0.1611(24)	0.6102(18)
O(10)	0.4380(21)	0.1349(20)	0.5409(21)
C(11)	0.9979(38)	0.2500	0.4180(37)
C(12)	0.9470(35)	0.1663(29)	0.5217(31)
C(12B)	0.9218(35)	0.1407(25)	0.3954(31)
C(13)	0.7913(16)	0.1200(10)	0.4744(11)
C(14)	0.7008(42)	0.1182(31)	0.3581(28)
C(14B)	0.6451(35)	0.1831(23)	0.4385(23)
C(15)	0.6117(41)	0.2500	0.3287(23)

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond distances and angles.

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