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Chemistry of iridium carbonyl cluster complexes. Synthesis, chemical characterization and X-ray crystal structures of $[PPh_4][Ir_6(CO)_{15}Cl] \cdot C_4H_8O$ and $[PPh_4][Ir_6(CO)_{14}Cl]$

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Abstract

The anion $[Ir_6(CO)_{15}Cl]^-$ has been formed by treating $[Ir_6(CO)_{15}]^{2-}$ with $FeCl_3$; $[Ir_6(CO)_{15}Cl]^-$ (**1**) is the first species formed, but if kept standing **1** slowly loses a CO ligand to give $[Ir_6(CO)_{14}Cl]^-$ (**2**). Compound **1** can also be obtained by treating $Ir_6(CO)_{16}$ with LiCl in anhydrous tetrahydrofuran, but, because of the long reaction time needed, a substantial amount of compound **2** is also formed. The crystal structures of $[PPh_4][Ir_6(CO)_{15}Cl] \cdot C_4H_8O$ (**1**) and $[PPh_4][Ir_6(CO)_{14}Cl]$ (**2**) have been determined. Anion **1** contains an octahedron of iridium atoms surrounded by eleven terminal, one edge, and three face-bridging carbonyl groups, and by one terminal chlorine atom. The disposition of the bridging carbonyl groups can be related to that of $Ir_6(CO)_{16}$ (red isomer) in which one face-bridging carbonyl group has become edge bridging. Selected bond distances are: Ir–Ir(average) 2.774, Ir–C(terminal, average) 1.85, Ir–C(edge bridging, average) 2.13, Ir–C(face bridging, average) 2.22, Ir–Cl 2.395(5) Å. Anion **2** contains a slightly distorted octahedron of iridium atoms bearing twelve terminal and two edge-bridging carbon monoxide groups; the chlorine atom bridges an Ir–Ir edge. The stereochemistry of anion **2** is related to that of $[Ir_6(CO)_{15}]^{2-}$ by replacing an edge-bridging carbonyl group by the μ-halogen atom [Cl bridges Ir(4)–Ir(3), C(13) bridges Ir(1)–Ir(6), C(14) bridges Ir(2)–Ir(3)]; i.e. each of the six iridium atoms is involved in only one bridge. Average selected bond distances are: Ir–Ir 2.767, Ir–C(terminal) 1.85, Ir–C(edge bridging) 2.05, Ir–Cl 2.484 Å.

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Introduction

There are several examples of transition metal carbonyl clusters in which halogen atoms or pseudohalogen groups are terminally bonded to one metal atom [1]. In the case of the cobalt subgroup metals, structurally characterized examples are: $[Co_4(CO)_{11}I]^-$ [2], $[Rh_5(CO)_{14}I]^{2-}$ [3], $[Rh_6(CO)_{15}I]^-$ [4], $[Ir_4(CO)_{11}X]^-$ (X = Br [5], SCN [6,7]). In contrast, there was only one example of a complex in which the halogen atom had been shown by X-ray diffraction to adopt a bridging coordination, namely $[Rh_7(CO)_{16}I]^{2-}$ [8], before we reported the characterization and the molecular structures of the isostructural iridium substituted carbonyl clusters $[Ir_6(CO)_{14}X]^-$ (X = Br, I or SCN) [9]. In the same paper we also described the chemical properties of the chloride analogue $[Ir_6(CO)_{14}Cl]^-$, and presented IR spectroscopic evidence for the intermediate formation of the unstable anions $[Ir_6(CO)_{15}X]^-$ (X = Cl, Br, I, or SCN) [9].

We have now been able to isolate some of these unstable anions, and we report here the synthesis and properties of $[Ir_6(CO)_{15}Cl]^-$ (**1**) and $[Ir_6(CO)_{14}Cl]^-$ (**2**). Both of the anions **1** and **2** have now been structurally characterized, and the crystal and molecular structures of $[PPh_4][Ir_6(CO)_{15}Cl] \cdot C_4H_8O$ and $[PPh_4][Ir_6(CO)_{14}Cl]$ are also presented for comparison.

Results and discussion

Synthesis and chemical behaviour of $[Ir_6(CO)_xCl]^-$ (x = 15: 1, 14: 2)

During a study of the reaction of $[Ir_6(CO)_{15}]^{2-}$ with several oxidizing agents, the hexanuclear dianion was treated with various molar ratios of $FeCl_3$ in tetrahydrofuran (THF) solution. IR spectroscopic monitoring showed that, when the molar ratio between $[Ir_6(CO)_{15}]^{2-}$ and $FeCl_3$ was ca. 1 : 2, an orange solution was formed that showed infrared absorption bands at 2043 (sh), 2035 (vs), 2020 (sh), 1975 (w), 1815 (m) cm^{-1}. (However, when this solution was kept its IR spectrum changed during ca. 2 days to that of $[Ir_6(CO)_{14}Cl]^-$ [9] and, sometimes traces of $[Ir_6(CO)_{15}]^{2-}$ were also formed.) Quick work-up of the initial orange solution followed by crystallization of the product from THF/cyclohexane, gave a mixture of orange and green crystals. The orange salt was shown by X-ray diffraction to be $[PPh_4][Ir_6(CO)_{15}Cl]$ (**1**). Figure 1a presents the IR spectrum of the selected orange crystals of **1**, which shows carbonyl stretching bands at 2044 (sh), 2037 (vs), 2017 (sh), 1978 (w), 1818 (m), 1787 (m, br) (cm^{-1}, THF solution) in accord with the presence of terminal and bridging CO groups, as found in the solid state structure (vide infra). The green crystals gave an IR spectrum (Fig. 1b) identical to that previously reported for $[PPh_4][Ir_6(CO)_{14}Cl]$ (**2**), with ν(CO) bands at 2069 (w), 2023 (vs), 1973 (mw) and 1823 (m) (cm^{-1}, THF solution) [9].

The formation of $[Ir_6(CO)_{15}Cl]^-$, in the reaction of $FeCl_3$ with $[Ir_6(CO)_{15}]^{2-}$ appears to involve the following formal stoichiometry:

$$[Ir_6(CO)_{15}]^{2-} + 2\ FeCl_3 \rightarrow [Ir_6(CO)_{15}Cl]^- + 2\ FeCl_2 + Cl^-$$

This reaction probably involves three steps: two one electron oxidations of the original cluster and then addition of the halide ligand. Electrochemical and spectroscopic experiments are in progress to elucidate the mechanism of the reaction, and, if possible, to characterize the intermediate species.

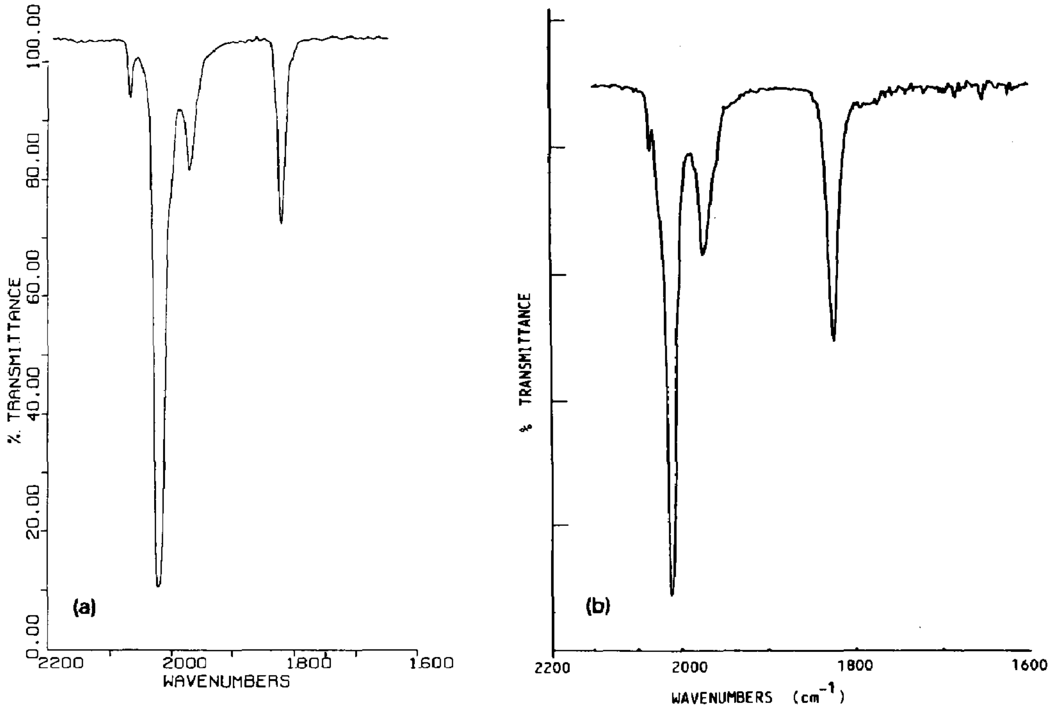

Fig. 1. (a) Infrared spectrum of [PPh_4][$Ir_6(CO)_{15}Cl$] (1) in THF solution; (b) Infrared spectrum of [PPh_4][$Ir_6(CO)_{14}Cl$] (2) in THF solution.

The red isomer of $Ir_6(CO)_{16}$ [10] reacts slowly with LiCl in a 1 : 4 molar ratio at room temperature in THF to give, after 6 h, a solution containing a mixture of anions **1** and **2**. This is due to the slowness of the reaction, which allows substantial decomposition of **1** to **2** to take place before the reaction of the starting carbonyl complex is complete, and after 24 h **2** can be notated almost quantitatively. Attempts to accelerate the reaction by increasing the amount of LiCl resulted in no appreciable improvement. A better ratio of compounds **1** and **2** could be only obtained by stopping the reaction after a short time, when some unchanged $Ir_6(CO)_{16}$ was present, making this approach inconvenient. Thus the best way to raise the proportion of **1** relative to that of **2** is to use the reaction with $FeCl_3$, which immediately gives a nearly pure solution of **1**, decomposition to **2** taking place only during the subsequent work-up and crystallization. Anion **2** was also obtained serendipitously during the attempt to crystallize $[HIr_6(CO)_{15}]^-$. We obtained NMR evidences for the presence of this derivative in solution, but the instability of this complex prevents its isolation. Anion $[HIr_6(CO)_{15}]^-$ was converted into anion **2** by reaction with CH_2Cl_2. We found that orange solutions of **1** under nitrogen are completely converted to deep green solutions of **2** within about 72 h at room temperature. Comparison of the IR spectra of compounds **1** and **2** shows that the carbon monoxide removal results in a shift of the IR bands to lower wavenumbers for the terminal CO groups, and this can be accounted in terms of an increased back donation towards the remaining carbon monoxide ligands.

The green derivative **2** is stable in solution under nitrogen as well as in the solid state, but if traces of water are present in the solution some decomposition to

Table 1

Fractional atomic coordinates for compound $[PPh_4][Ir_6(CO)_{15}Cl]\cdot C_4H_8O$ (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ir(1)	0.24231(6)	−0.01803(6)	0.29761(6)
Ir(2)	0.31104(6)	0.16236(6)	0.22242(7)
Ir(3)	0.35014(6)	0.03395(7)	0.08595(7)
Ir(4)	0.27974(6)	−0.14680(6)	0.16293(7)
Ir(5)	0.45020(6)	0.05033(7)	0.26392(7)
Ir(6)	0.14084(6)	−0.03411(6)	0.12045(7)
Cl	0.1116(4)	0.0351(4)	0.3581(5)
P	0.8601(4)	0.6503(4)	0.4266(4)
O(1)	0.276(1)	−0.142(1)	0.439(1)
O(2)	0.150(1)	0.269(1)	0.251(1)
O(3)	0.504(1)	0.378(1)	0.245(1)
O(4)	0.277(1)	−0.098(1)	−0.103(1)
O(5)	0.548(1)	0.224(1)	0.065(1)
O(6)	0.175(1)	−0.320(2)	−0.006(2)
O(7)	0.326(1)	−0.298(1)	0.276(1)
O(8)	0.667(1)	0.238(1)	0.277(1)
O(9)	0.546(1)	−0.039(1)	0.411(1)
O(10)	−0.055(1)	0.017(1)	0.150(1)
O(11)	0.010(1)	−0.201(1)	−0.052(1)
O(12)	0.4007(9)	0.200(1)	0.429(1)
O(13)	0.037(1)	−0.238(1)	0.205(1)
O(14)	0.2009(9)	0.157(1)	0.019(1)
O(15)	0.513(1)	−0.093(1)	0.127(1)
C(1)	0.262(2)	−0.095(2)	0.387(2)
C(2)	0.211(1)	0.231(2)	0.240(2)
C(3)	0.428(1)	0.294(2)	0.235(2)
C(4)	0.306(1)	−0.047(2)	−0.031(2)
C(5)	0.471(2)	0.151(2)	0.072(2)
C(6)	0.217(2)	−0.252(2)	0.061(2)
C(7)	0.307(1)	−0.240(2)	0.233(2)
C(8)	0.584(1)	0.167(2)	0.274(2)
C(9)	0.514(1)	−0.001(2)	0.356(2)
C(10)	0.021(1)	0.002(2)	0.137(2)
C(11)	0.055(2)	−0.137(2)	0.014(2)
C(12)	0.358(1)	0.140(2)	0.361(2)
C(13)	0.113(1)	−0.156(2)	0.208(2)
C(14)	0.226(1)	0.105(2)	0.073(2)
C(15)	0.449(1)	−0.064(1)	0.152(2)
C(111)	0.973(1)	0.754(1)	0.515(1)
C(112)	1.010(1)	0.728(1)	0.595(2)
C(113)	1.099(2)	0.807(2)	0.664(2)
C(114)	1.153(2)	0.905(2)	0.644(2)
C(115)	1.121(1)	0.935(2)	0.569(2)
C(116)	1.031(1)	0.862(2)	0.502(2)
C(121)	0.768(1)	0.558(1)	0.477(2)
C(122)	0.723(1)	0.602(2)	0.539(2)
C(123)	0.642(2)	0.533(2)	0.574(2)
C(124)	0.617(2)	0.420(2)	0.549(2)
C(125)	0.661(2)	0.376(2)	0.494(2)
C(126)	0.740(1)	0.444(1)	0.456(2)
C(131)	0.913(1)	0.575(1)	0.355(1)
C(132)	1.029(1)	0.597(2)	0.379(2)

Table 1 (continued)

Atom	x	y	z
C(133)	1.067(2)	0.538(2)	0.318(2)
C(134)	0.996(2)	0.464(2)	0.248(2)
C(135)	0.885(2)	0.443(2)	0.226(2)
C(136)	0.844(1)	0.501(1)	0.280(2)
C(141)	0.784(1)	0.707(1)	0.353(2)
C(142)	0.826(2)	0.750(2)	0.288(2)
C(143)	0.764(2)	0.790(2)	0.231(2)
C(144)	0.664(2)	0.785(2)	0.237(2)
C(145)	0.632(2)	0.758(2)	0.303(2)
C(146)	0.687(2)	0.712(2)	0.366(2)
O(200)	0.794(2)	0.579(3)	0.022(3)
C(201)	0.795(4)	0.537(4)	−0.086(4)
C(202)	0.680(4)	0.506(4)	−0.123(4)
C(203)	0.620(5)	0.454(5)	−0.080(5)
C(204)	0.659(4)	0.523(4)	0.019(4)

$[Ir_6(CO)_{15}]^{2-}$ is observed. Compound **2** is not reconverted into compound **1** when subjected to 1 atm of carbon monoxide; there are examples of metal cluster carbonyls which lose and take up carbon monoxide reversibly [11,12].

Crystal and molecular structures of $[PPh_4][Ir_6(CO)_{15}Cl] \cdot C_4H_8O$ *(1) and* $[PPh_4][Ir_6(CO)_{14}(\mu\text{-}Cl)]$ *(2)*

The crystal structures of compounds **1** and **2** involve discrete anions and cations and one THF molecule of solvation, in the case of complex **1**. No unusual bond lengths and angles in the counter ions and no short contacts between atoms of different ionic fragments were found. The positional parameters for complexes **1** and **2** are listed in Table 1 and 2, respectively. Selected bond distances and angles are listed in Table 3 and 4 for **1** and Table 5 and 6 for **2**. The ORTEP drawing of the whole structure of the two monoanions and the scheme used for labelling atoms are illustrated in Fig. 2 for **1** and Fig. 3 for **2**. In order to classify the different types of carbon monoxide groups, we have assumed a maximum value of ca. 2.45 Å for a bonding, though weak, Ir–C interaction.

As shown in Figs. 2 and 3, for both complexes the geometries of the metal frameworks are based on a slightly distorted octahedral cluster of iridium atoms. Anion **1** contains eleven terminal, one edge, and three face-bridging carbonyl groups and one terminally bonded chlorine atom. In anion **1** except for Ir(1), which bears the terminally-bonded chlorine atom, each iridium atom is bonded to two terminal carbon monoxide groups. The edge-bridging carbonyl CO(12) links Ir(1) and Ir(2), whereas the face-bridging ligand CO(14) links the Ir(2), Ir(3), Ir(6) face; CO(15) links the Ir(3), Ir(4), Ir(5) face; and CO(13) links the Ir(1), Ir(4), Ir(6) face. The disposition of the bridging carbonyl groups can be viewed as that of $Ir_6(CO)_{16}$, red isomer [10], in which one face-bridging CO has become edge-bridging in **1**. This bridging carbonyl group is asymmetric with an average Ir–C distance of 2.13 Å. The three face-bridging carbonyl groups are all asymmetric, with Ir–C distances ranging from 2.08(2) to 2.41(2) Å, and an average value of 2.22 Å. This value falls in the usual range for anionic hexanuclear carbonyl clusters [13–15]. The metal–metal

Table 2

Fractional atomic coordinates for compound $[PPh_4][Ir_6(CO)_{14}Cl]$ (**2**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ir(1)	−0.3370(1)	−0.6175(1)	0.0460(1)
Ir(2)	−0.3413(1)	−0.6301(1)	0.1588(1)
Ir(3)	−0.1392(1)	−0.6067(1)	0.1639(1)
Ir(4)	−0.2589(1)	−0.4664(1)	0.1123(1)
Ir(5)	−0.1330(1)	−0.5813(1)	0.0533(1)
Ir(6)	−0.2100(1)	−0.7549(1)	0.0919(1)
Cl	−0.1304(9)	−0.3902(7)	0.0532(4)
C(1)	−0.3373(29)	−0.5571(24)	−0.0190(13)
O(1)	−0.3480(29)	−0.5223(24)	−0.0650(13)
C(2)	−0.4716(34)	−0.6487(27)	0.0524(16)
O(2)	−0.5494(25)	−0.6831(21)	0.0595(11)
C(3)	−0.4066(34)	−0.7477(30)	0.1868(16)
O(3)	−0.4462(28)	−0.8148(24)	0.2046(13)
C(4)	−0.4500(33)	−0.5558(27)	0.1744(15)
O(4)	−0.5210(23)	−0.4991(18)	0.1843(10)
C(5)	−0.0333(40)	−0.5085(34)	0.1819(19)
O(5)	0.0113(29)	−0.4409(24)	0.1922(13)
C(6)	−0.0582(37)	−0.7146(32)	0.1921(17)
O(6)	−0.0280(28)	−0.7872(24)	0.2079(13)
C(7)	−0.2549(35)	−0.3927(30)	0.1745(17)
O(7)	−0.2568(27)	−0.3449(22)	0.2170(12)
C(8)	−0.3722(34)	−0.4085(27)	0.0790(15)
O(8)	−0.4441(23)	−0.3677(19)	0.0686(10)
C(9)	−0.1281(31)	−0.6187(26)	−0.0173(15)
O(9)	−0.1248(25)	−0.6332(21)	−0.0622(12)
C(10)	−0.0008(33)	−0.6047(26)	0.0654(15)
O(10)	0.0794(29)	−0.6380(23)	0.0762(13)
C(11)	−0.1047(33)	−0.8238(28)	0.0682(15)
O(11)	−0.0256(28)	−0.8684(23)	0.0525(13)
C(12)	−0.2562(36)	−0.8704(31)	0.1245(17)
O(12)	−0.2910(30)	−0.9452(26)	0.1456(14)
C(13)	−0.2986(28)	−0.7664(23)	0.0264(13)
O(13)	−0.3197(22)	−0.8243(19)	−0.0082(10)
C(14)	−0.2488(26)	−0.6113(22)	0.2234(13)
O(14)	−0.2519(23)	−0.6019(18)	0.2687(11)
P	−0.7363(8)	0.0227(7)	0.1225(3)
C(51)	−0.2737(29)	−0.1362(24)	0.8314(14)
C(52)	−0.2963(32)	−0.1159(28)	0.7799(15)
C(53)	−0.3092(34)	−0.2097(29)	0.7491(16)
C(54)	−0.2916(39)	−0.3091(33)	0.7741(18)
C(55)	−0.2700(38)	−0.3251(32)	0.8315(19)
C(56)	−0.2599(29)	−0.2306(24)	0.8608(13)
C(21)	−0.1394(26)	0.0301(21)	0.8698(12)
C(22)	−0.0772(30)	−0.0037(24)	0.8295(14)
C(23)	0.0138(32)	0.0391(26)	0.8192(14)
C(24)	0.0380(36)	0.1233(30)	0.8515(17)
C(25)	−0.0213(37)	0.1581(31)	0.8925(18)
C(26)	−0.1066(31)	0.1095(26)	0.9083(14)
C(31)	−0.2923(28)	−0.0636(23)	0.9465(12)
C(32)	−0.2177(35)	−0.0850(28)	0.9761(17)
C(33)	−0.2135(43)	−0.1113(36)	1.0315(22)

Table 2 (continued)

Atom	x	y	z
C(34)	−0.3237(39)	−0.1281(32)	1.0490(19)
C(35)	−0.3969(37)	−0.1121(31)	1.0151(18)
C(36)	−0.3831(33)	−0.0725(27)	0.9644(15)
C(41)	−0.3535(26)	0.0740(22)	0.8567(12)
C(42)	−0.3382(30)	0.1779(25)	0.8618(14)
C(43)	−0.4120(36)	0.2486(31)	0.8472(16)
C(44)	−0.4984(33)	0.2084(27)	0.8286(15)
C(45)	−0.5236(34)	0.1032(27)	0.8270(16)
C(46)	−0.4442(30)	0.0332(25)	0.8429(14)

distances range from 2.756(1) to 2.803(1) Å, with an average value of 2.774 Å, a value in agreement with those in the complexes $[Ir_6(CO)_{14}X]^-$ (X = Br, I, or SCN) [9]. It is noteworthy that the extreme values differ from the average by only about 1%, and both refer to unbridged bonds. The terminal Ir(1)–Cl distance of 2.395(5) Å is in the usual range for organometallic iridium compounds, although comparison can only be made with the bond lengths in mononuclear iridium complexes, because this is the first example of a chlorine-substituted iridium carbonyl cluster [16]. The distances of the chlorine atom from the adjacent metal atoms Ir(2) and Ir(6) are greater than the sum of the Van der Waals radii of iridium and chlorine, thus ruling

Table 3

Interatomic distances (Å) within the anion $[Ir_6(CO)_{15}Cl]^-$ (1) with estimated standard deviations

Ir(1)–Ir(2)	2.760(1)	Ir(2)–C(12)	2.21(2)
Ir(1)–Ir(4)	2.760(1)	Ir(1)–C(13)	2.08(2)
Ir(1)–Ir(5)	2.756(1)	Ir(4)–C(13)	2.41(2)
Ir(1)–Ir(6)	2.767(1)	Ir(6)–C(13)	2.25(2)
Ir(2)–Ir(3)	2.790(1)	Ir(2)–C(14)	2.27(2)
Ir(2)–Ir(5)	2.796(1)	Ir(3)–C(14)	2.16(2)
Ir(2)–Ir(6)	2.763(1)	Ir(6)–C(14)	2.11(2)
Ir(3)–Ir(4)	2.783(1)	Ir(3)–C(15)	2.36(2)
Ir(3)–Ir(5)	2.772(1)	Ir(4)–C(15)	2.17(2)
Ir(3)–Ir(6)	2.779(1)	Ir(5)–C(15)	2.15(2)
Ir(4)–Ir(5)	2.765(1)	C(1)–O(1)	1.12(2)
Ir(4)–Ir(6)	2.803(1)	C(2)–O(2)	1.13(2)
Ir(1)–Cl	2.395(5)	C(3)–O(3)	1.17(2)
Ir(1)–C(1)	1.87(3)	C(4)–O(4)	1.14(2)
Ir(2)–C(2)	1.90(2)	C(5)–O(5)	1.16(2)
Ir(2)–C(3)	1.83(2)	C(6)–O(6)	1.17(3)
Ir(3)–C(4)	1.85(2)	C(7)–O(7)	1.15(2)
Ir(3)–C(5)	1.87(2)	C(8)–O(8)	1.16(2)
Ir(4)–C(6)	1.78(3)	C(9)–O(9)	1.13(2)
Ir(4)–C(7)	1.85(2)	C(10)–O(10)	1.14(2)
Ir(5)–C(8)	1.84(2)	C(11)–O(11)	1.14(2)
Ir(5)–C(9)	1.86(2)	C(12)–O(12)	1.15(2)
Ir(6)–C(10)	1.88(2)	C(13)–O(13)	1.18(2)
Ir(6)–C(11)	1.84(2)	C(14)–O(14)	1.23(2)
Ir(1)–C(12)	2.06(2)	C(15)–O(15)	1.16(2)

Table 4

Angles (deg) within the anion $[Ir_6(CO)_{15}Cl]^-$ (**1**) with estimated standard deviations in parentheses

Terminal CO			
Ir(1)–C(1)–O(1)	178(2)	Ir(4)–C(7)–O(7)	178(2)
Ir(2)–C(2)–O(2)	178(2)	Ir(5)–C(8)–O(8)	177(2)
Ir(2)–C(3)–O(3)	178(2)	Ir(5)–C(9)–O(9)	175(2)
Ir(3)–C(4)–O(4)	179(2)	Ir(6)–C(10)–O(10)	175(2)
Ir(3)–C(5)–O(5)	178(2)	Ir(6)–C(11)–O(11)	174(2)
Ir(4)–C(6)–O(6)	179(2)		
Bridging CO			
Ir(1)–C(12)–Ir(2)	80.4(8)	Ir(3)–C(14)–Ir(6)	81.1(7)
Ir(1)–C(12)–O(12)	143(2)	Ir(2)–C(14)–O(14)	130(1)
Ir(2)–C(12)–O(12)	133(2)	Ir(3)–C(14)–O(14)	131(2)
Ir(1)–C(13)–Ir(4)	75.4(6)	Ir(6)–C(14)–O(14)	137(1)
Ir(1)–C(13)–Ir(6)	79.3(7)	Ir(3)–C(15)–Ir(4)	75.6(5)
Ir(4)–C(13)–Ir(6)	73.9(6)	Ir(3)–C(15)–Ir(5)	75.7(5)
Ir(1)–C(13)–O(13)	142(2)	Ir(4)–C(15)–Ir(5)	79.5(6)
Ir(6)–C(13)–O(13)	133(2)	Ir(3)–C(15)–O(15)	129(2)
Ir(4)–C(13)–O(13)	126(1)		
Ir(2)–C(14)–Ir(3)	78.0(7)	Ir(4)–C(15)–O(15)	135(1)
Ir(2)–C(14)–Ir(6)	78.1(8)	Ir(5)–C(15)–O(15)	138(1)

out interaction between the halogen and these two metal atoms (in other words, the Ir(1)–Cl bond is truly terminal).

Anion **2** is isostructural with the analogous derivatives $[Ir_6(CO)_{14}(\mu\text{-}X)]^-$ (X = Br, I, SCN) [9] and contains twelve terminal (two for each metal atom), two edge-bridg-

Table 5

Interatomic distances (Å) within the anion $[Ir_6(CO)_{14}Cl]^-$ (**2**) with estimated standard deviations in parentheses

Ir(1)–Ir(2)	2.810(2)	Ir(5)–C(9)	1.82(4)
Ir(1)–Ir(4)	2.774(2)	Ir(5)–C(10)	1.83(4)
Ir(1)–Ir(5)	2.785(3)	Ir(6)–C(11)	1.78(4)
Ir(1)–Ir(6)	2.724(2)	Ir(6)–C(12)	1.82(4)
Ir(2)–Ir(3)	2.734(3)	Ir(1)–C(13)	2.07(3)
Ir(2)–Ir(4)	2.670(2)	Ir(6)–C(13)	2.02(3)
Ir(2)–Ir(6)	2.922(2)	Ir(2)–C(14)	2.04(3)
Ir(3)–Ir(4)	2.751(2)	Ir(3)–C(14)	2.09(3)
Ir(3)–Ir(5)	2.771(2)	C(1)–O(1)	1.24(4)
Ir(3)–Ir(6)	2.798(2)	C(2)–O(2)	1.15(5)
Ir(4)–Ir(5)	2.695(2)	C(3)–O(3)	1.12(4)
Ir(5)–Ir(6)	2.669(2)	C(4)–O(4)	1.23(4)
Ir(4)–Cl	2.476(11)	C(5)–O(5)	1.10(5)
Ir(5)–Cl	2.493(9)	C(6)–O(6)	1.10(5)
Ir(1)–C(1)	1.80(3)	C(7)–O(7)	1.23(4)
Ir(1)–C(2)	1.86(5)	C(8)–O(8)	1.13(4)
Ir(2)–C(3)	1.90(4)	C(9)–O(9)	1.13(1)
Ir(2)–C(4)	1.80(4)	C(10)–O(10)	1.19(5)
Ir(3)–C(5)	1.97(5)	C(11)–O(11)	1.27(5)
Ir(3)–C(6)	1.91(5)	C(12)–O(12)	1.20(5)
Ir(4)–C(7)	1.82(4)	C(13)–O(13)	1.18(4)
Ir(4)–C(8)	1.89(4)	C(14)–O(14)	1.13(3)

Table 6

Angles (deg) within the anion $[Ir_6(CO)_{14}Cl]^-$ (2) with estimated standard deviations in parentheses

Terminal CO			
Ir(1)–C(1)–O(1)	172(4)	Ir(4)–C(7)–O(7)	177(4)
Ir(2)–C(2)–O(2)	169(4)	Ir(4)–C(8)–O(8)	167(4)
Ir(2)–C(3)–O(3)	178(4)	Ir(5)–C(9)–O(9)	174(3)
Ir(2)–C(4)–O(4)	176(3)	Ir(5)–C(10)–O(10)	168(3)
Ir(3)–C(5)–O(5)	166(5)	Ir(6)–C(11)–O(11)	176(3)
Ir(3)–C(6)–O(6)	167(5)	Ir(6)–C(12)–O(12)	177(4)
Bridging CO			
Ir(1)–C(13)–Ir(6)	84(1)	Ir(2)–C(14)–Ir(3)	83(1)
Ir(1)–C(13)–O(13)	136(3)	Ir(2)–C(14)–O(14)	140(3)
Ir(6)–C(13)–O(13)	141(3)	Ir(3)–C(14)–O(14)	137(3)
Bridging Chlorine			
Ir(4)–Cl–Ir(5)	65.7(3)	Ir(5)–Ir(4)–Cl	57.5(2)
Ir(4)–Ir(5)–Cl	56.9(3)		

ing carbonyl groups and one edge-bridging chlorine atom. The average distances Ir–Ir 2.759 Å, Ir–C(terminal) 1.85, and Ir–C(bridging) 2.05 Å are almost identical with those found in the isostructural compounds [9]. The average Ir–Cl distance, 2.485 Å, is very close to that in the chlorine-bridged iridium complexes [16].

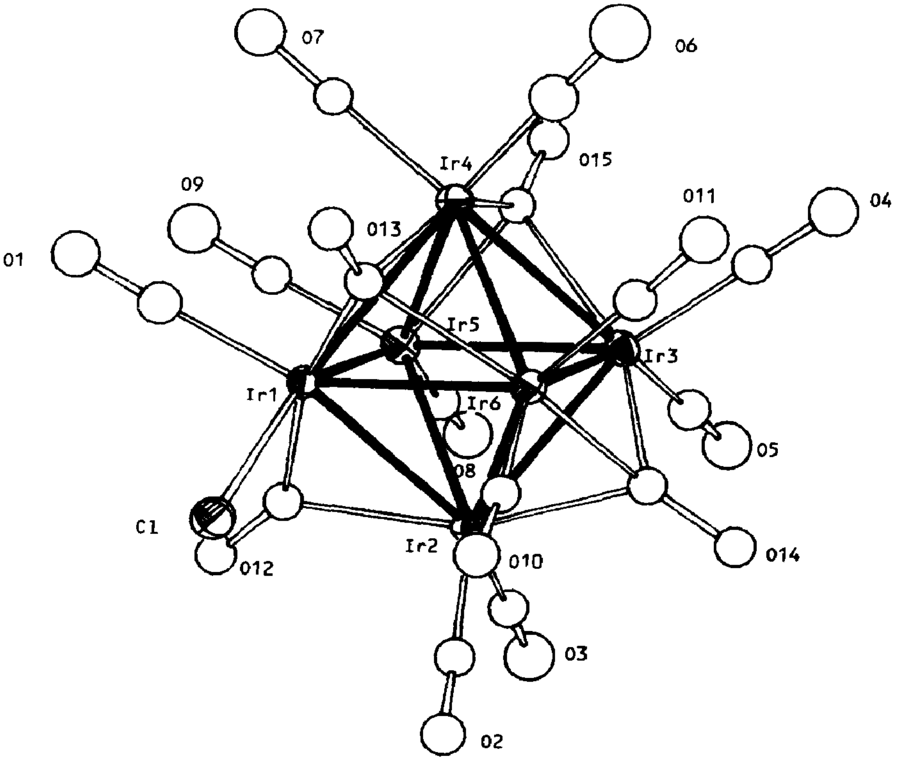

Fig. 2. ORTEP drawing of anion 1. Thermal ellipsoids are drawn at 30% probability.

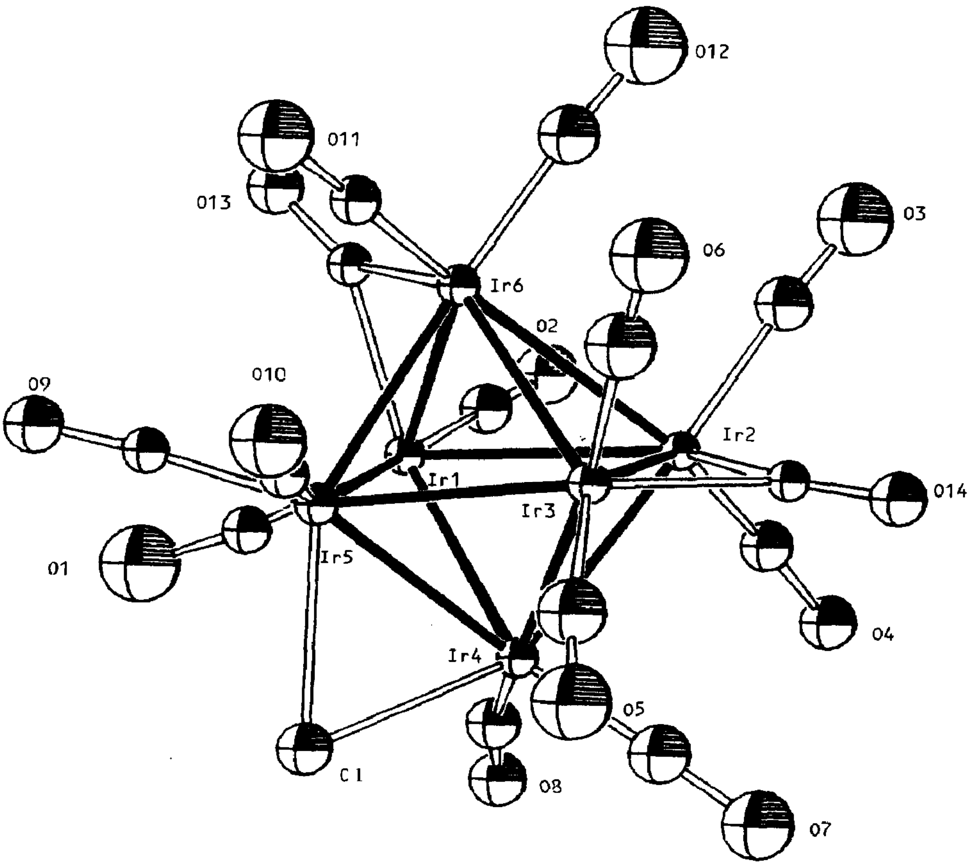

Fig. 3. ORTEP drawing of anion 2. Thermal ellipsoids are drawn at 30% probability.

From Table 7 it can be seen that, in general, substitution of a bridging CO group of $[Ir_6(CO)_{15}]^{2-}$ with a μ-X group leads to a marked decrease in the Ir–Ir distances, accompanied by a significant spreading of their distribution, as measured by the Q values (see Table 7). On the other hand, substitution of a terminal CO of $Ir_6(CO)_{16}$ (red isomer) leads, for X = COEt, or CO_2Me, to expansion of the cluster, with evident distortions from ideality, though weaker than those found in μ-halide or pseudohalide substituted derivatives.

When the large number of neutral [10,17,18], anionic [9,13–15] and metal capped [19,20], octahedra of iridium are considered, it is evident that the most stable steric arrangement of the ligands around the metallic framework is the one which contains twelve terminal (two for each metal atom) and three or four bridging groups, in many different dispositions [21 *]. In addition to the frequently invoked charge equalization and interligand repulsion effects, packing forces in the crystal lattice are also relevant in determining the final geometry of the ligands. For iridium carbonyl clusters, cases of isomerism in the solid state are well documented [6,7,12] so that it must be questioned whether the structure found in the crystal really represents the most stable isomer, or only is merely one of the many different quasi

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* Reference number with asterisk indicates a note in the list of references.

Table 7

Synoptic table for Ir–Ir distances in octahedral iridium carbonyl clusters and their anionic derivatives

Compound	Ir–Ir [e]	min	max	Q [f]	ref.
$Ir_6(CO)_{16}$ [a]	2.779	2.775(1)	2.783(1)	0.1	10
$Ir_6(CO)_{16}$ [b]	2.784	2.751(1)	2.810(1)	1.2	10
$[Ir_6(CO)_{15}]^{2-}$	2.773	2.730(1)	2.822(1)	1.8	13
$[Ir_6(CO)_{15}CO_2Me]^-$	2.793	2.703(1)	2.870(1)	3.2	15
$[Ir_6(CO)_{15}COEt]^-$	2.790	2.690(1)	2.870(1)	3.6	14
$[Ir_6(CO)_{15}Cl]^-$	2.774	2.756(1)	2.803(1)	1.0	this work
$[Ir_6(CO)_{14}Cl]^-$	2.759	2.669(2)	2.922(2)	5.9	this work
$[Ir_6(CO)_{14}Br]^-$	2.760	2.621(1)	2.938(1)	6.4	9
$[Ir_6(CO)_{14}I]^-$	2.760	2.668(1)	2.885(1)	4.5	9
$[Ir_6(CO)_{14}SCN]^-$ [c]	2.758	2.682(2)	2.841(2)	3.0	9
$[Ir_6(CO)_{14}SCN]^-$ [d]	2.759	2.683(2)	2.835(2)	2.8	9

[a] red isomer. [b] black isomer. [c,d] independent molecules in the same crystal. [e] average Ir–Ir bond distances. [f] Q is the relative maximum absolute difference between each observed and average Ir–Ir bond distances, defined by

$$Q=\frac{100*\max_{i,j}\left[(\mathrm{Ir}_i-\mathrm{Ir}_j)-(\mathrm{Ir}-\mathrm{Ir})_{\mathrm{avg}}\right]}{(\mathrm{Ir}-\mathrm{Ir})_{\mathrm{avg}}}.$$

iso-energetic structures which undergo interconversion in solution by fluxional processes [22]. The structure of $[Ir_6(CO)_{15}Cl]^-$ is related to that of $[Rh_6(CO)_{15}I]^-$ [4], in which the basic structure of $Rh_6(CO)_{16}$ is retained, the only change arising from the simple tilting of one of the face-bridging carbon monoxide groups toward an edge bridging position.

$[Ir_6(CO)_{15}Cl]^-$ and $[Ir_6(CO)_{14}Cl]^-$ are both 86 e^- clusters and obey Wade's rule for octahedral clusters [23]. In compound **2** the bridging chlorine must be regarded as a 3-electron donor, and for this complex the overall electron count is again maintained. Thus, in effect, in the bridging an extra lone pair from the chlorine ligand, displaces a carbonyl group.

Experimental

All solvents were purified and dried by conventional methods and stored under nitrogen. All reactions were carried out under oxygen-free nitrogen by Schlenk-tube techniques [24]. $Ir_6(CO)_{16}$ (red isomer) was prepared as previously described in [10]. Infrared spectra were recorded on a Perkin-Elmer 781 spectrophotometer using calcium fluoride cells previously purged with N_2.

Preparation of $[PPh_4][Ir_6(CO)_{15}Cl]\cdot C_4H_8O$ *(1)*

(a) A 0.1 *M* solution of $FeCl_3$ was prepared by dissolving 0.32 g of anhydrous $FeCl_3$ in 20 cm^3 of THF. A round-bottomed flask equipped with a dropping funnel was carefully evacuated, filled with nitrogen, and charged with a solution of $[PPh_4]_2[Ir_6(CO)_{15}]$ (0.312 g, 0.14 mmol) in THF (20 cm^3). The $FeCl_3$ solution was added dropwise, the mixture being monitored by IR spectroscopy during the addition. After the addition of about 3 cm^3 of the $FeCl_3$ solution, the spectrum revealed the presence of a new compound and complete disappearance of the starting material. The solution was evaporated to dryness and the pale-yellow residue washed with water (2×10 cm^3) and 2-propanol (3×5 cm^3). The crude product was dissolved in THF (3 cm^3) and the solution carefully layered with cyclohexane (15 cm^3). After a few days, flat crystals of $[PPh_4][Ir_6(CO)_{15}Cl] \cdot C_4H_8O$ had formed. The mother liquor was removed with syringe, and the crystals washed with hexane (2×20 cm^3) and dried. Yield 0.11 g (40%).

(b) A stirred suspension of $Ir_6(CO)_{16}$ (0.546 g, 0.34 mmol) in THF (25 cm^3) was treated with LiCl (0.057 g, 1.34 mmol). The reaction was monitored by IR spectroscopy until the spectrum clearly showed the formation of $[Ir_6(CO)_{15}Cl]^-$ (ca. 6 h). The solution was filtered to remove some $Ir_6(CO)_{16}$ and a solution of $[N(PPh_3)_2]Cl$ (0.40 g, 0.70 mmol) in 2-propanol (40 cm^3) was added. The solution was concentrated in vacuo and the THF partly removed, to give a precipitate of compound **1**. Yield 0.330 g (36%).

Preparation of $[PPh_4][Ir_6(CO)_{14}Cl]$ (2)

A stirred suspension of $Ir_6(CO)_{16}$ (0.712 g, 0.445 mmol) in THF (30 cm^3) was treated with LiCl (0.075 g, 1.77 mmol). IR monitoring showed that $[Ir_6(CO)_{15}Cl]^-$ (**1**) was initially formed and slowly changed to $[Ir_6(CO)_{14}Cl]^-$ (**2**); the reaction was complete after 24 h. The product was recovered by adding a 2-propanol (50 cm^3) solution of $[PPh_4]Cl$ (0.70 g, 1.9 mmol) to the green THF solution and concentrating the mixture in vacuo. The solid product was filtered off, washed first with 2-propanol then with n-hexane, and vacuum dried. Yield 0.699 g (82%). Crystals of $[PPh_4][Ir_6(CO)_{14}Cl]$ were obtained by layering cyclohexane over a CH_2Cl_2 solution of the cluster. The compound is soluble, and stable under a nitrogen atmosphere for a few days, in anhydrous CH_2Cl_2, $CHCl_3$, THF and MeCN, sparingly soluble in 2-propanol, and insoluble in aliphatic and aromatic hydrocarbons.

Transformation of 1 into 2

In a typical preparation $[PPh_4][Ir_6(CO)_{15}Cl]$ (0.203 g, 1.04 mmol) was dissolved in THF (10 cm^3) under nitrogen. The solution, which gradually changed from orange to deep green, was repeatedly evaporated (once a day) to dryness under vacuum and the green solid redissolved in 10 cm^3 of THF (ca. 4 times). The IR spectrum revealed that there had been complete transformation to $[PPh_4][Ir_6(CO)_{14}Cl]$. The compound was crystallized by layering cyclohexane over a concentrated CH_2Cl_2 solution.

X-ray analysis: intensity data collection, structure solution and refinement

Compound **1**: crystal data and other experimental details are summarized in Table 8. Intensity data were collected on an Enraf-Nonius CAD-4 automated diffractometer using Mo-K_α radiation ($\lambda = 0.71073$ Å) with a graphite crystal monochromator in the incident beam. Standard CAD-4 setting, indexing and data collection programs were used. Three check reflections were monitored at 100-reflection intervals throughout data collection and showed that was a 40% crystal decay (based on F_o) from the beginning to the end of data collection. Lorentz, polarization, decay and absorption corrections were applied, the latter performed with the empirical method described in ref. 25. The structure solution was carried out by direct methods (MULTAN) [26] and difference Fourier syntheses, and the refinement by full-matrix least-squares, the minimized function being $\Sigma w(F_o - k|F_c|)^2$.

Table 8

Summary of crystal data and intensity collection parameters for complexes **1** and **2**

Compound	$[PPh_4][Ir_6Cl(CO)_{15}]\cdot C_4H_8O$	$[PPh_4][Ir_6(CO)_{14}Cl]$
Formula	$C_{43}H_{28}ClIr_6O_{16}P$	$C_{38}H_{20}ClIr_6O_{14}P$
Mol.wt (g/mole)	2020.32	1920.2
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a, Å	13.249(5)	13.428(24)
b, Å	13.316(4)	13.047(6)
c, Å	15.609(5)	24.850(10)
α, °	98.06(3)	
β, °	101.43(3)	90.14(11)
γ, °	111.06(3)	
U, Å^3	2451(4)	4354(11)
Z	2	4
$F(000)$	1816	3416
Calc. density g cm^{-3}	2.733	2.929
μ(Mo-K_α), cm^{-1}	162.93	183.64
Crystal dimensions (mm)	0.20×0.10×0.08	0.30×0.50×0.30
Scan mode	ω	$\theta/2\theta$
θ range, deg.	3–23	3–22.5
Octants in the reciprocal space explored	$\pm h, \pm k, +l$	$+h, +k, \pm l$
Measured reflections	6713	5867
Unique observed reflections ($I > 3\sigma(I)$)	3265	2661
No. of variables	309	271
final R, R_w [a]	0.041, 0.046	0.053, 0.046

[a] $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$; $R_w = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{1/2}$

Individual weights were given as $w = 1/\sigma^2(F_o)$ where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{1/2}/Lp$ and p the "ignorance factor" equal to 0.03. Scattering factors and anomalous dispersion corrections were taken from ref. 27. The final difference Fourier maps showed only peaks, not > 0.6 e/Å^3, near to the metal atoms. All computations were carried out on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package (SDP) and the physical constants therein tabulated [28], and ORTEP [29] for drawings.

Compound **2**: crystal data and other experimental details are summarized in Table 8. Although $[PPh_4][Ir_6(CO)_{14}Br]$ and $[PPh_4][Ir_6(CO)_{14}Cl]$ are isostructural the crystals of the two compounds are not isomorphous. Intensity data were collected in a similar manner as for compound **1**, except that (i) a Siemens/Nicolet/Syntex P2$_1$ diffractometer was used; and (ii) no crystal decay was observed. The positions of the six iridium atoms were determined by direct methods (SHELX86) [31], and the rest of the atoms located from difference-Fourier maps and refined by full-matrix least-squares.

Tables of thermal parameters, and hydrogen atom coordinates (where relevant), complete lists of bond lengths and angles, and lists of observed and calculated structure factors are available from the authors.

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