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Chemistry of iridium carbonyl cluster complexes. Synthesis, chemical characterization and solid state structure of the mixed-metal carbonyl cluster $[PPh_4][Ir_6(\mu\text{-}CO)_3(CO)_{12}\{\mu_3\text{-}Cu(NCMe)\}] \cdot CH_2Cl_2$ and its conversion to the dianion $[Ir_{12}(CO)_{26}]^{2-}$

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Abstract

The cluster $[Ir_6(CO)_{15}\{Cu(NCMe)\}]^-$ is obtained by condensation of $[Ir_6(CO)_{15}]^{2-}$ with $[Cu(NCMe)_4]^+$ at room temperature in tetrahydrofuran. The salt $[PPh_4][Ir_6(CO)_{15}\{\mu_3\text{-}Cu(NCMe)\}] \cdot CH_2Cl_2$ crystallizes in the monoclinic space group $P2_1/n$ (non-standard no. 14) with $a = 21.146(12)$, $b = 11.512(9)$, $c = 20.450(9)$ Å, $\beta = 90.58(4)°$, and $Z = 4$; $R = 0.038$ and $R_w = 0.041$ for 2175 observed reflections having $I \geq 3\sigma(I)$. The monoanion consists of an octahedron of iridium atoms, face-capped by the CuNCMe group, with twelve terminal carbonyls (two for each iridium atom) and three edge-bridging carbonyls. Average distances (Å) and angles are: Ir–Ir, 2.779; Ir–Cu, 2.636; Ir–C_t, 1.82; C–O_t, 1.18; Ir–C–O_t, 173°; Ir–C_b, 2.02; C–O_b, 1.19; Ir–C–O_b, 138° (t = terminal, b = edge-bridging). In solution the mixed metal carbonyl cluster decomposes slightly and slowly by loss of copper metal and formation of the previously reported $[Ir_{12}(CO)_{26}]^{2-}$.

Introduction

In an earlier paper, we described the reactivity, the spectroscopic properties and the solid state structure of the first large anionic iridium carbonyl cluster $[Ir_{12}(CO)_{26}]^{2-}$, obtained by reaction of $[Ir_6(CO)_{15}]^{2-}$ and $[Cu(NCMe)_4]^+$. It can be represented as three face-fused stacked metal octahedra [1].

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Subsequently we prepared two mixed-metal carbonyl clusters, by reaction of $[Ir_6(CO)_{15}]^{2-}$ with the two isolobal fragments $[HgCl]^+$ and $[AuPPh_3]^+$. The two anions $[Ir_6(CO)_{15}(HgCl)]^-$ and $[Ir_6(CO)_{15}(AuPPh_3)]^-$ were characterized by a combination of analytical and diffractometric techniques. These contain octahedral iridium frames face-capped by the heteroatoms [2]. Although the X-ray analyses showed some differences in the architecture of the bridging carbonyl ligands, their IR and ^{13}C NMR spectra were strikingly similar, indicating similar structures in solution.

Meanwhile, we realized that the reactivity toward nucleophiles described for $[Ir_{12}(CO)_{26}]^{2-}$ [1] is rather peculiar for a high nuclearity carbonyl cluster [3], and very like that observed for the two heptanuclear mixed metal carbonyl clusters. Additionally, we noticed that the reported infrared spectrum of the dodecametal cluster is almost superposable in shape and position, on those of the two heptanuclear complexes. Therefore we decided to reinvestigate the $[Ir_6(CO)_{15}]^{2-}$/$[Cu(NCMe)_4]^+$ system with great care.

In this paper we report the synthesis and the chemical characterization of $[Ir_6(CO)_{15}\{Cu(NCMe)\}]^-$ and the X-ray structural analysis of the salt $[PPh_4][Ir_6(CO)_{15}\{Cu(NCMe)\}] \cdot CH_2Cl_2$. The fluxional behaviour of $[Ir_6(CO)_{15}\{Cu(NCMe)\}]^-$ has been studied by ^{13}C NMR spectroscopy.

Results and discussion

Synthesis of $[Ir_6(CO)_{15}\{Cu(NCMe)\}]^-$

The condensation of $[Cu(NCMe)_4]^+$ with $[Ir_6(CO)_{15}]^{2-}$ is performed in tetrahydrofuran (THF) solution at room temperature and, as soon as the reagents are mixed and dissolved, quantitative formation of $[Ir_6(CO)_{15}\{Cu(NCMe)\}]^-$ (**1**) is observed. The infrared spectrum of the reaction mixture is identical with that of selected crystals of $[PPh_4][Ir_6(CO)_{15}\{Cu(NCMe)\}] \cdot CH_2Cl_2$ (**1A**) and shows bands, in the carbonyl stretching region, at 2057w, 2008vs, 1945m and 1799s cm^{-1} in THF (Fig. 1(a)), attributable to terminal and edge-bridging carbonyls. The compounds $[Ir_6(CO)_{15}(HgCl)]^-$ (**2**) and $[Ir_6(CO)_{15}(Au\text{-}PPh_3)]^-$ (**3**) show infrared stretching bands very similar to that of **1** in shape and position [4*]: the main difference is associated with the absorptions at 1765m cm^{-1} (compound **2**) and at 1790m cm^{-1} (compound **3**) indicative of face- and asymmetric edge-bridging carbonyl groups, respectively. The 1799 cm^{-1} band of **1** indicates the presence of true edge-bridging carbonyls, in agreement with the solid state structure (see below). No infrared bands could be assigned to the coordinated MeCN. The presence of the MeCN group is however confirmed by the ^1H NMR spectrum, which shows a resonance at 2.25 ppm (CH_2Cl_2-d_2 solution), with the correct ratio 3:20 to the cation phenyl hydrogens of the salt $[PPh_4][Ir_6(CO)_{15}\{Cu(NCMe)\}]$.

The capping group can be easily removed from the cluster by a variety of nucleophiles, such as halides or hydroxide ions; the parent $[Ir_6(CO)_{15}]^{2-}$ can be also regenerated upon dissolving **1** in acetonitrile. These reactions were previously attributed to $[Ir_{12}(CO)_{26}]^{2-}$, which was erroneously considered a very reactive species [1].

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

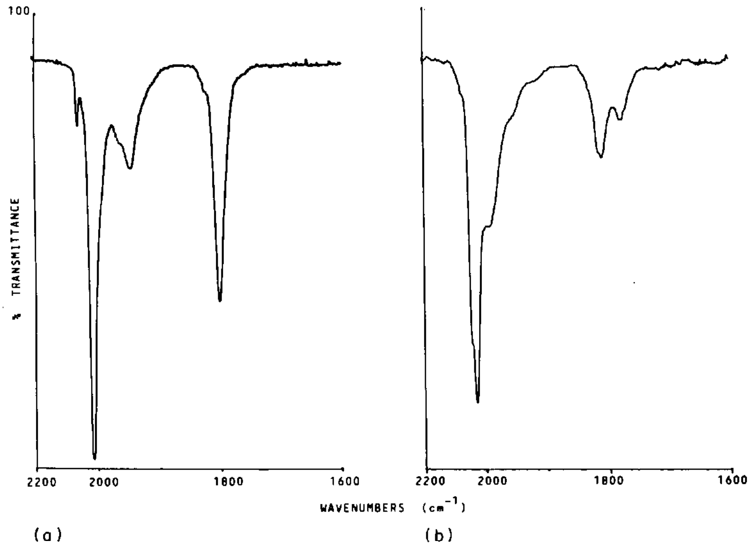

Fig. 1. (a) IR spectrum of $[PPh_4][Ir_6(CO)_{15}\{Cu(NCMe)\}]$ in THF solution. (b) IR spectrum of $[PPh_4]_2[Ir_{12}(CO)_{26}]$ in MeCN solution.

If **1** is allowed to stand in a THF or CH_2Cl_2 solution, at room temperature, for several days a metallic deposit of copper is observed, and **1** is partially oxidized to $[Ir_{12}(CO)_{26}]^{2-}$ (**4**); the salts of **4** with different bulky cations are almost insoluble in THF and can be separated by filtration. The salt $[PPh_4]_2[Ir_{12}(CO)_{26}]$ is soluble in MeCN or acetone and solutions of selected crystals show absorption bands at 2042sh, 2029vs, 1993m, 1810m and 1780w cm^{-1} in MeCN solution (Fig. 1(b)).

The transformation of $[Ir_6(CO)_{15}\{Cu(NCMe)\}]^-$ into (**4**) is extremely slow, and, as judged by the infrared spectra of the solution, stops after a while; thus, $[Ir_{12}(CO)_{26}]^{2-}$ is produced in very small quantities. In the attempt to obtain a complete transformation of **1** into **4**, we heated a THF solution of **1** under reflux for several hours, but obtained a different cluster, probably through the decarbonylation of $[Ir_{12}(CO)_{26}]^{2-}$; this new compound is presently under investigation.

The reaction of $[Ir_6(CO)_{15}]^{2-}$ with other oxidants was also tested [5], but we could obtain $[Ir_{12}(CO)_{26}]^{2-}$ only when using $[Cu(NCMe)_4]PF_6$. $[PPh_4]$-$[Ir_6(CO)_{15}\{Cu(NCMe)\}]$ can be crystallized from CH_2Cl_2 by slow diffusion of pentane; to avoid as much as possible the undesired transformation of the complex, the solution must be kept at low temperature (−20°C).

In spite of its small yield, the formation of **4** is very reproducible and crystals of the salts of this compound with different bulky cations could always be isolated, and a full X-ray data set was collected for $[NEt_4]_2[Ir_{12}(CO)_{26}]$ (see below) [6*].

Solid state structure of $[PPh_4][Ir_6(\mu\text{-}CO)_3(CO)_{12}\{\mu_3\text{-}Cu(NCMe)\}]\cdot CH_2Cl_2$ *(1A)*

The structure of **1A** consists of an ionic packing of $[Ir_6(CO)_{15}\{Cu(NCMe)\}]^-$ cluster anions and tetraphenylphosphonium cations containing clathrated CH_2Cl_2 molecules with normal van der Waals' interactions. The solvent molecules are probably responsible for the poor stability of the crystals even under an inert

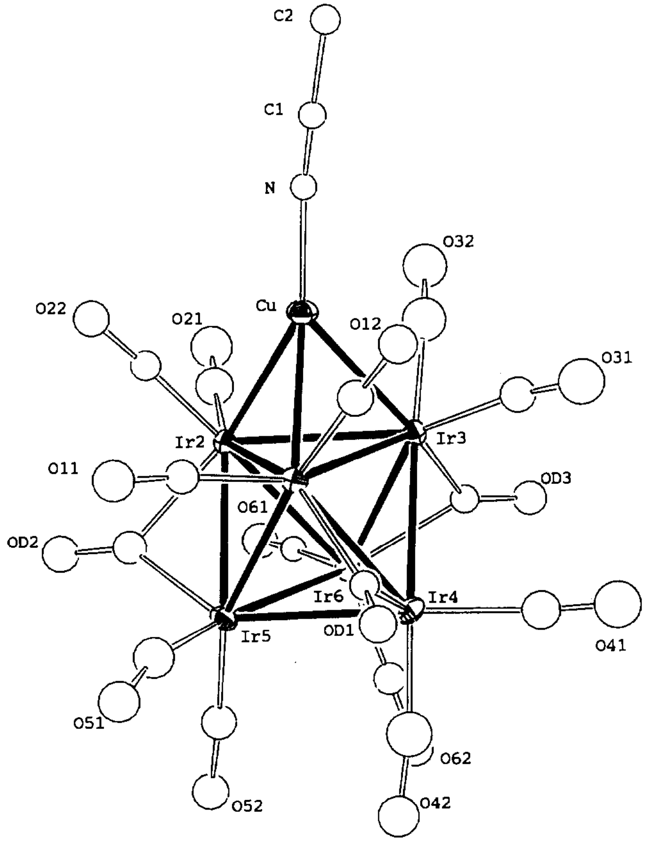

Fig. 2. ORTEP drawing of $[Ir_6(CO)_{15}\{Cu(NCMe)\}]^-$. Thermal ellipsoids are drawn at the 30% probability level.

atmosphere. An ORTEP drawing of the cluster anion is shown in Fig. 2, while relevant bond distances and angles are collected in Tables 1 and 2, respectively.

The metal skeleton of **1** consists of a slightly distorted octahedron of iridium atoms capped by a μ_3-Cu atom bearing a terminally bonded MeCN ligand. The idealized symmetry of the Ir_6Cu core is C_{3v}, while the whole anion belongs to the C_3 point group. Therefore, according to the presence of the idealized three fold axis the Ir–Ir bond distances (minimum 2.711(2) Å, maximum 2.839(2) Å, average 2.779 Å) can be divided into four distinct sets, which are, however, not as different as their nature would induce one to expect: these are those involving only the Ir(1), Ir(2) and Ir(3) atoms (layer 1, average 2.809 Å), those involving only the Ir(4), Ir(5) and Ir(6) atoms (layer 2, average 2.768 Å), carbonyl unbridged and bridged interlayer interactions (average 2.812 Å and 2.727 Å, respectively).

The Ir–Cu distances (average 2.636 Å) strictly can be compared only with those of the unique Ir–Cu cluster so far structurally characterized (average 2.87 Å) [7], although the larger number of the lighter copper atoms and the presence of phosphine ligands, instead of carbonyls, makes the analogy weak. Similarly, the widely varying Ir–Cu distances of the few known oligonuclear mixed-metal com-

Table 1

Bond distances (Å) in the monoanion $[Ir_6(CO)_{15}\{Cu(NCMe)\}]^-$ with estimated standard deviations (e.s.d.s) of the last digit in parentheses

Ir(1)-Ir(2)	2.793(2)	Ir(2)-C(21)	1.79(5)
Ir(1)-Ir(3)	2.824(2)	Ir(2)-C(22)	1.79(3)
Ir(1)-Ir(4)	2.736(2)	Ir(3)-C(31)	1.85(4)
Ir(1)-Ir(5)	2.804(2)	Ir(3)-C(32)	1.88(5)
Ir(2)-Ir(3)	2.811(2)	Ir(4)-C(41)	1.90(5)
Ir(2)-Ir(5)	2.734(2)	Ir(4)-C(42)	1.79(5)
Ir(2)-Ir(6)	2.839(2)	Ir(5)-C(51)	1.76(4)
Ir(3)-Ir(4)	2.794(2)	Ir(5)-C(52)	1.79(3)
Ir(3)-Ir(6)	2.711(2)	Ir(6)-C(61)	1.83(3)
Ir(4)-Ir(5)	2.762(2)	Ir(6)-C(62)	1.80(3)
Ir(4)-Ir(6)	2.775(2)	C(D1)-O(D1)	1.21(3)
Ir(5)-Ir(6)	2.767(2)	C(D2)-O(D2)	1.18(4)
Ir(1)-Cu	2.646(4)	C(D3)-O(D3)	1.17(3)
Ir(2)-Cu	2.645(4)	C(11)-O(11)	1.11(4)
Ir(3)-Cu	2.617(4)	C(12)-O(12)	1.19(4)
Cu-N	1.89(2)	C(21)-O(21)	1.18(4)
N-C(1)	1.09(3)	C(22)-O(22)	1.18(3)
C(1)-C(2)	1.45(4)	C(31)-O(31)	1.15(4)
Ir(1)-C(D1)	1.95(3)	C(32)-O(32)	1.22(5)
Ir(2)-C(D2)	2.10(4)	C(41)-O(41)	1.12(5)
Ir(3)-C(D3)	2.03(3)	C(42)-O(42)	1.20(4)
Ir(4)-C(D1)	1.99(3)	C(51)-O(51)	1.27(4)
Ir(5)-C(D2)	2.02(4)	C(52)-O(52)	1.23(3)
Ir(6)-C(D3)	2.02(3)	C(61)-O(61)	1.14(3)
Ir(1)-C(11)	1.89(4)	C(62)-O(62)	1.19(3)
Ir(1)-C(12)	1.81(4)		

plexes [8], which contain a variety of ligands and geometries, mean that no meaningful comparison can be carried out.

Of the 15 carbonyl ligands, 12 are terminally bonded, two on each iridium atom (average values are: Ir-C 1.82 Å, C-O 1.18 Å and Ir-C-O 173°), and three span alternate interlayer edges (average values are: Ir-C 2.02 Å, C-O 1.19 Å and Ir-C-O 138°), in a fashion very similar to that found in the parent $[Ir_6(CO)_{15}]^{2-}$ [9] and in $[Ir_6(CO)_{15}(AuPPh_3)]^-$ [2]. In the latter compound, however, 'semitriple' bridging carbonyls were found, whereas the bridging carbonyl ligands in **1** are definitely edge-bridging, the shorter non-bonding Ir-C(bridging) distance being 3.20 Å.

The bonding parameters of the acetonitrile ligand (Cu-N = 1.89(2) Å, N-C(1) = 1.09(3) Å, C(1)-C(2) = 1.45(4) Å and Cu-N-C(1) 173(3)°, N-C(1)-C(2) = 179(3)°) are in agreement with a linearly coordinated molecule slightly bent from the ideal threefold axis passing through the copper atom and the centre of the Ir_6 octahedron; the slight asymmetry of the Ir-Cu bond distances, together with intermolecular packing effects might account for this.

We decided to perform a second structural analysis of the salt $[NEt_4]_2$-$[Ir_{12}(CO)_{26}]$ (**4A**) [6*] since isomerism is not unusual in iridium carbonyl clusters [10] and in large anionic carbonyl clusters, [3,11] probably due to crystal packing interactions. The structural parameters of (**4A**) are very similar to those of the previously reported $[PPh_4]_2[Ir_{12}(CO)_{26}]$ salts. This probably indicates the intrinsic

Table 2

Bond angles (deg.) in the monoanion $[Ir_6(CO)_{15}\{Cu(NCMe)\}]^-$ with e.s.d.s of the last digit in parentheses

Ir(2)-Ir(1)-Ir(3)	60.05(5)	Ir(4)-Ir(1)-Cu	117.4(1)
Ir(2)-Ir(1)-Ir(4)	90.76(5)	Ir(5)-Ir(1)-Cu	116.5(1)
Ir(2)-Ir(1)-Ir(5)	58.48(5)	Ir(1)-Ir(2)-Cu	58.1(1)
Ir(3)-Ir(1)-Ir(4)	60.31(5)	Ir(3)-Ir(2)-Cu	57.2(1)
Ir(3)-Ir(1)-Ir(5)	88.02(5)	Ir(5)-Ir(2)-Cu	118.9(1)
Ir(4)-Ir(1)-Ir(5)	59.80(5)	Ir(6)-Ir(2)-Cu	114.6(1)
Ir(1)-Ir(2)-Ir(3)	60.51(5)	Ir(1)-Ir(3)-Cu	58.04(9)
Ir(1)-Ir(2)-Ir(5)	60.96(5)	Ir(2)-Ir(3)-Cu	58.2(1)
Ir(1)-Ir(2)-Ir(6)	88.82(5)	Ir(4)-Ir(3)-Cu	116.3(1)
Ir(3)-Ir(2)-Ir(5)	89.67(6)	Ir(6)-Ir(3)-Cu	120.0(1)
Ir(3)-Ir(2)-Ir(6)	57.35(4)	Ir(1)-Cu-Ir(2)	63.73(9)
Ir(5)-Ir(2)-Ir(6)	59.51(5)	Ir(1)-Cu-Ir(3)	64.89(9)
Ir(1)-Ir(3)-Ir(2)	59.43(5)	Ir(2)-Cu-Ir(3)	64.56(9)
Ir(1)-Ir(3)-Ir(4)	58.28(5)	Ir(1)-Cu-N	138.3(7)
Ir(1)-Ir(3)-Ir(6)	90.79(5)	Ir(2)-Cu-N	148.3(8)
Ir(2)-Ir(3)-Ir(4)	89.21(6)	Ir(3)-Cu-N	139(7)
Ir(2)-Ir(3)-Ir(6)	61.85(5)	Ir(1)-C(D1)-Ir(4)	88(1)
Ir(4)-Ir(3)-Ir(6)	60.52(5)	Ir(1)-C(D1)-O(D1)	139(3)
Ir(1)-Ir(4)-Ir(3)	61.41(5)	Ir(4)-C(D1)-O(D1)	133(3)
Ir(1)-Ir(4)-Ir(5)	61.33(5)	Ir(2)-C(D2)-Ir(5)	83(2)
Ir(1)-Ir(4)-Ir(6)	91.33(6)	Ir(2)-C(D2)-O(D2)	133(3)
Ir(3)-Ir(4)-Ir(5)	89.46(6)	Ir(5)-C(D2)-O(D2)	144(3)
Ir(3)-Ir(4)-Ir(6)	58.26(5)	Ir(3)-C(D3)-Ir(6)	84(1)
Ir(5)-Ir(4)-Ir(6)	59.97(5)	Ir(3)-C(D3)-O(D3)	138(3)
Ir(1)-Ir(5)-Ir(2)	60.56(5)	Ir(6)-C(D3)-O(D3)	138(2)
Ir(1)-Ir(5)-Ir(4)	58.87(5)	Ir(1)-C(11)-O(11)	175(3)
Ir(1)-Ir(5)-Ir(6)	90.05(5)	Ir(1)-C(12)-O(12)	178(3)
Ir(2)-Ir(5)-Ir(4)	91.46(6)	Ir(2)-C(21)-O(21)	176(4)
Ir(2)-Ir(5)-Ir(6)	62.13(5)	Ir(2)-C(22)-O(22)	176(3)
Ir(4)-Ir(5)-Ir(6)	60.24(5)	Ir(3)-C(31)-O(31)	171(4)
Ir(2)-Ir(6)-Ir(3)	60.81(5)	Ir(3)-C(32)-O(32)	159(4)
Ir(2)-Ir(6)-Ir(4)	89.02(5)	Ir(4)-C(41)-O(41)	174(4)
Ir(2)-Ir(6)-Ir(5)	58.36(5)	Ir(4)-C(42)-O(42)	173(4)
Ir(3)-Ir(6)-Ir(4)	61.22(5)	Ir(5)-C(51)-O(51)	165(4)
Ir(3)-Ir(6)-Ir(5)	91.08(5)	Ir(5)-C(52)-O(52)	176(3)
Ir(4)-Ir(6)-Ir(5)	59.78(5)	Ir(6)-C(61)-O(61)	177(3)
Ir(2)-Ir(1)-Cu	58.1(1)	Ir(6)-C(62)-O(62)	175(3)
Ir(3)-Ir(1)-Cu	57.07(9)		

stability of their stereogeometry, which has a carbonyl arrangement closely related to that of the parent $[Ir_6(CO)_{15}]^{2-}$ cluster [1,9].

^{13}C *NMR studies*

A variable temperature study of the $^{13}C\{^1H\}$ NMR spectra of **1** (*ca.* 30% ^{13}CO enriched, THF-d_8 solution) was undertaken in order to compare its spectroscopic properties with those of the homologous derivatives **2** and **3** and, also, to prove its stability and ascertain the nature of the species present in solution. ^{13}C NMR spectra for **1** at several temperatures are shown in Fig. 3.

The ^{13}C NMR spectrum of a solution of the cluster, kept at −20°C for 10 days, was identical to that obtained immediately after dissolving the sample in the solvent, with no trace of transformation of **1** into **4**.

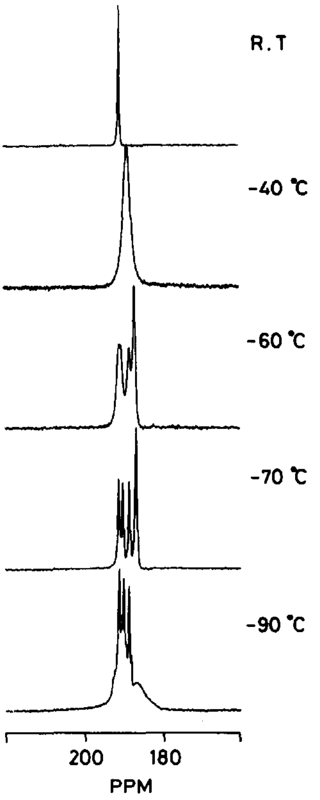

Fig. 3. Variable temperature ^{13}C NMR spectra.

The limiting low-temperature ^{13}C NMR spectrum of 1 should show five equally intense signals, corresponding to the five sets of non-equivalent carbonyls expected from the C_3 symmetry of the anion as found in the solid state structure. However, at −70°C, the ^{13}C NMR spectrum contains only four sharp signals at 190.9, 189.9, 188.2 and 186.4 ppm, of relative intensity 1 : 1 : 1 : 2. The most striking feature of this spectrum is that all the signals lie in a very narrow range, preventing a full assignment of the resonances. The similarity of the chemical shifts is even more peculiar considering that one of the signals should belong to edge-bridging carbonyl groups; usually the ^{13}C chemical shifts of this type of ligand are well separated from those of the terminal carbonyl groups [12], and in the case of iridium monoanionic octahedral carbonyl clusters lie at about 210 ppm [2]. Therefore, the chemical shifts found in this NMR spectrum suggest a molecule possessing terminal carbonyl groups only, inconsistent with the number of signals (see below).

The peak with intensity 2 at 186.4 ppm can be assigned to the terminal carbonyl groups bonded to the copper-capped face of the octahedron, analogous to the case of $[Ir_6(CO)_{15}\{Au(PPh_3)\}]^-$ [2]. At −90°C, the lowest temperature which we could reach without freezing the solution, the same number of signals were observed, but the signal at 186.4 ppm was much broader, indicating that two truly non-equivalent sets of carbonyl groups were averaging at a lower rate; such a scrambling can involve the migration of the bridging ligands around the threefold axis, possibly via μ_3-CO, mimicking C_{3v} symmetry on the NMR timescale [13*]. At this temperature, a second set of weak signals appears at 190.3, 189.2 and 187.9 ppm, and they probably belong to a different isomer frozen out at this temperature. These signals cannot be assigned to the face-bridged structure, because the two isomers interconvert at a lower rate than the two sets of terminal carbonyls and also because there is no trace of any other signal which can be reasonably assigned to the μ_3-CO ligands; they could be attributed to the isomer with only terminal ligands [14*]. Upon raising the temperature to −60°C, a simultaneous broadening of all the signals occurs, and at −30°C all the carbon monoxide ligands became equivalent on the NMR timescale, giving rise to a single broad peak at 188.4 ppm (calculated average value 188.4 ppm), indicating a complete scrambling of all the ligands around the metal frame. This resonance is sharp and is shifted slightly to 190.2 ppm at room temperature.

The limiting process can be accounted for either by a merry-go-round movement of the ligands around the faces of the cluster, or by a migration of the heteroatom between two opposite faces, associated with terminal-bridging interchanges [15]. In the monoanions **2** and **3**, we observed two distinct fluxional processes, at two different temperatures, involving first the terminal carbon monoxide groups, and then all the ligands. Considering the fluxional behaviour of the clusters **2**, **3** and **1**, a clear trend can be outlined: on moving from a structure containing a μ_3-CO group compound **2**, via compound **3** with asymmetric carbonyl groups to compound **1** with μ-CO ligands. The two fluxional processes commence at more similar temperatures and complete scrambling requires a lower activation energy.

Two-dimensional ^{13}C exchange spectra (NOESY) were recorded on **1** at −70°C and −60°C. The spectrum at the lower temperature does not show any cross-peak, indicating the absence of any ligand scrambling. At the higher temperature (Fig. 4) only one pair of signals, (at 189.9 ppm and 188.2 ppm) do not give rise to a cross-peak: this weak evidence suggests that these two signals are assignable to axial and bridging carbonyl groups, which cannot interconvert directly.

Conclusions

From the present reinvestigation of the reaction of $[Ir_6(CO)_{15}]^{2-}$ with $[Cu(NCMe)_4]^+$ we have demonstrated that **1** is a relatively stable compound, is the main product present in solution and that the reactivity previously reported for **4** must be attributed to **1** [1]. A solution of **1** is oxidized to $[Ir_{12}(CO)_{26}]^{2-}$, in a very small amount, with the formation of copper metal.

In spite of the fact that **1** is present in solution in a much higher amount than **4**, the different solubilities favour the crystallization of the far less soluble salts of the dodecametal cluster. Most of the salts of $[Ir_6(CO)_{15}\{Cu(NCMe)\}]^-$ crystallize with great difficulty, and usually form sticky materials on precipitation, containing nice crystals of $[Ir_{12}(CO)_{26}]^{2-}$; great care was therefore necessary in order to obtain single crystals of **1** suitable for X-ray analysis, to fully confirm our hypotheses.

Experimental

All the solvents were purified and dried by conventional methods and stored under nitrogen. All the reactions were carried out under an oxygen-free nitrogen

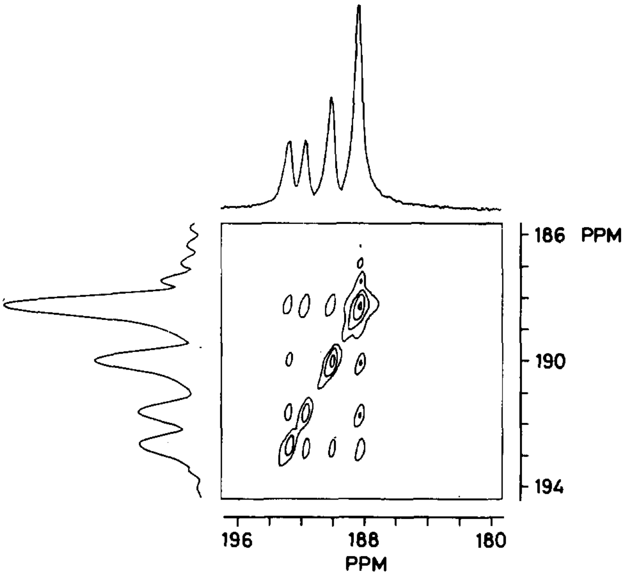

Fig. 4. HNSC 2D spectrum at −60°C.

atmosphere using Schlenk technique [16]. $[Ir_6(CO)_{15}]^{2-}$ and $[Cu(NCMe)_4]PF_6$ were prepared as already described [17,18]. IR spectra were recorded on a Perkin–Elmer 781 grating spectrophotometer using calcium fluoride cells previously purged with N_2. ^1H NMR spectra and variable-temperature $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC200 spectrometer operating at 200 MHz, for protons, 50.3 MHz for carbon and are reported relative to the external standard $SiMe_4$. The 2D ^{13}C NOESY experiment was performed by using a 1K × 512 data matrix with a mixing time of 50 ms.

Preparation of $[PPh_4][Ir_6(CO)_{15}\{\mu_3\text{-}Cu(NCMe)\}]$ *(1A)*

In a Schlenk tube are placed $[PPh_4]_2[Ir_6(CO)_{15}]$ (0.11 g, 0.049 mmol) and THF (5 cm^3). When the solid is dissolved, $[Cu(NCMe)_4]PF_6$ (0.020 g, 0.053 mmol) is added in one portion. After 10 min, the completeness of the reaction is checked by IR and a further small amount of $[Cu(NCMe)_4]PF_6$ is added. The solution is then filtered to remove most of the $[PPh_4]PF_6$ salt, and taken to dryness in vacuum. The residue is dissolved in CH_2Cl_2 (4 cm^3) and layered with pentane (20 cm^3). The slow diffusion of the two solvents was performed at low temperature (−20°C) yielding 0.052 g (51%) of $[PPh_4][Ir_6(CO)_{15}\{Cu(NCMe)\}] \cdot CH_2Cl_2$. Anal. Found: C, 24.41; H, 0.99; N, 0.75. $C_{42}H_{25}Cl_2CuIr_6NPO_{15}$ calc.: C, 23.99; H, 1.20; N, 0.67%.

Preparation of $[PPh_4]_2[Ir_{12}(CO)_{26}]$

A solution of $[PPh_4]_2[Ir_6(CO)_{15}]$ (0.77 g, 0.34 mmol) in THF (15 cm^3) was treated with $[Cu(NCMe)_4]PF_6$ (0.14 g, 0.37 mmol) and stirred for 30 min at room temperature. The solvent was removed in vacuum and the solid was washed with 2-propanol (10 cm^3). The residue was dissolved in THF (20 cm^3), filtered, and layered with cyclohexane. After complete inter-diffusion of the two layers, the mother liquor was removed with a syringe and the semi-solid material (mainly

Table 3

Crystal data and data collection parameters for $[PPh_4][Ir_6(CO)_{15}\{Cu(NCMe)\}]\cdot CH_2Cl_2$ (**1A**)

Empirical formula	$C_{42}H_{25}Cl_2CuIr_6NO_{15}P$	Scan range (deg)	$1.0+0.35 \tan \theta$
Formula weight (amu)	2102.29	Prescan speed (deg min^{-1})	20
Crystal system	Monoclinic	Prescan acceptance $\sigma(I)/I$	0.80
Space group	$P2_1/n$ (non-standard No. 14)	Required $\sigma(I)/I$	0.02
a (Å)	21.146(12)	Max. scan time (s)	40
b (Å)	11.512(9)	Collected octants	$h, k, \pm l$
c (Å)	20.450(9)	No. collected reflexions	5861
β (deg)	90.58(4)	No. unique observed reflexions ($I > 3\sigma(I)$)	2175
V (Å^3)	4978(9)	Crystal decay	25% on F_o
Z	4	No. of reflexions for abs. corr.	3
D_{calc} (g cm^{-3})	2.805	Min. transmission factor	0.44
$F(000)$	3776	Crystal dimensions (mm)	0.27×0.28×0.32
Radiation Mo-K_α (Å)	= 0.71073	Fudge factor p	0.04
Diffractometer	CAD-4 Enraf-Nonius	No. of ref. variables	323
μ (cm^{-1})	165.4	R [a]	0.038
θ range (deg)	3–21	R_w [a]	0.041
Scan method	ω	GOF [b]	1.257
		Max. peak final diff. Fourier, (e Å^{-3})	1.12

[a] $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$ and $R_w = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{1/2}$. [b] $GOF = [\Sigma w(F_o - k|F_c|)^2/(N_{observations} - N_{variables})]^{1/2}$.

composed of $[PPh_4][Ir_6(CO)_{15}Cu(NCMe)]$) was extracted with THF (10 cm^3), leaving as a residue some amount of copper metal and a few crystals of $[PPh_4]_2[Ir_{12}(CO)_{26}]$, soluble in acetone.

X-Ray crystal structure determination of 1A

Crystal data and experimental conditions are summarized in Table 3. A dark prismatic crystal of approximate dimensions 0.27 × 0.28 × 0.32 mm was mounted in a Lindemann glass capillary tube, sealed under nitrogen and placed on a goniometer head. The intensity data were collected on an Enraf–Nonius CAD4 automated diffractometer using Mo-K_α radiation. A least-squares fit of 25 randomly oriented intense reflections with θ ranging from 8° to 12° provided the unit cell parameters. Intensities were collected using a variable scan range with a 25% extension at each end for background determination. Three standard reflections were measured at regular intervals and showed a constant decay of the scattering power of the crystal which was evaluated about 25% (on F_o) at the end of the data collection. The full data set was therefore corrected for decay as well as for Lorentz and polarization effects. An empirical absorption correction was performed based on psi-scans (psi 0–360°, every 10°) of three suitable reflections with χ values close to 90° [19].

The structure was solved by conventional three-dimensional Patterson and Fourier difference methods and refined by full-matrix least-squares using the Enraf–Nonius Structure Determination Package (SDP) and the physical constants tabulated therein on a PDP 11/73 computer [20]. Individual weights were assigned

Table 4

Fractional atomic coordinates for $[PPh_4][Ir_6(CO)_{15}\{Cu(NCMe)\}]\cdot CH_2Cl_2$ with e.s.d.s in parentheses [a]

Atom	*x*	*y*	*z*
Ir(1)	0.82447(6)	0.1955(1)	0.56323(6)
Ir(2)	0.73734(6)	0.0240(1)	0.59715(6)
Ir(3)	0.71570(6)	0.2553(1)	0.63478(6)
Ir(4)	0.73078(6)	0.3237(1)	0.50480(7)
Ir(5)	0.74420(6)	0.0935(1)	0.46958(6)
Ir(6)	0.64003(6)	0.1623(1)	0.54065(6)
Cu	0.8075(2)	0.1318(4)	0.6861(2)
P	0.6034(4)	0.1808(9)	0.1598(4)
O(D1)	0.862(1)	0.380(2)	0.469(1)
O(D2)	0.721(1)	−0.165(2)	0.495(1)
O(D3)	0.581(1)	0.338(2)	0.630(1)
O(11)	0.932(1)	0.047(2)	0.518(1)
O(12)	0.904(1)	0.337(2)	0.656(1)
O(21)	0.647(1)	−0.101(3)	0.682(1)
O(22)	0.849(1)	−0.110(2)	0.644(1)
O(31)	0.762(1)	0.484(3)	0.685(1)
O(32)	0.668(1)	0.173(3)	0.767(1)
O(41)	0.709(1)	0.573(3)	0.543(1)
O(42)	0.698(1)	0.360(2)	0.364(1)
O(51)	0.855(1)	0.073(2)	0.380(1)
O(52)	0.650(1)	0.070(2)	0.358(1)
O(61)	0.551(1)	−0.032(2)	0.563(1)
O(62)	0.559(1)	0.263(2)	0.434(1)
N	0.855(1)	0.123(2)	0.765(1)
C(1)	0.883(1)	0.130(3)	0.810(1)
C(2)	0.920(1)	0.140(3)	0.870(1)
C(D1)	0.825(1)	0.323(3)	0.500(1)
C(D2)	0.732(2)	−0.067(3)	0.508(2)
C(D3)	0.623(1)	0.280(3)	0.612(1)
C(11)	0.893(2)	0.102(3)	0.537(2)
C(12)	0.872(2)	0.279(3)	0.620(2)
C(21)	0.682(2)	−0.054(4)	0.646(2)
C(22)	0.803(1)	−0.058(3)	0.627(1)
C(31)	0.743(2)	0.394(3)	0.671(2)
C(32)	0.697(2)	0.213(4)	0.721(2)
C(41)	0.713(2)	0.480(4)	0.527(2)
C(42)	0.708(2)	0.351(4)	0.422(2)
C(51)	0.811(2)	0.068(4)	0.421(2)
C(52)	0.688(2)	0.083(3)	0.404(2)
C(61)	0.585(1)	0.042(3)	0.556(1)
C(62)	0.594(1)	0.226(3)	0.475(2)
C(111)	0.597(1)	0.166(3)	0.074(1)
C(112)	0.650(1)	0.186(3)	0.034(1)
C(113)	0.645(1)	0.173(3)	−0.034(1)
C(114)	0.585(1)	0.155(3)	−0.063(1)
C(115)	0.529(2)	0.143(3)	−0.024(2)
C(116)	0.536(1)	0.152(3)	0.046(2)
C(121)	0.562(1)	0.060(3)	0.194(1)
C(122)	0.576(1)	−0.051(3)	0.167(1)
C(123)	0.546(1)	−0.153(3)	0.189(1)
C(124)	0.504(2)	−0.135(3)	0.239(2)
C(125)	0.491(1)	−0.027(3)	0.269(2)
C(126)	0.521(2)	0.069(3)	0.248(2)

Table 4 (continued)

Atom	x	y	z
C(131)	0.687(1)	0.184(3)	0.184(1)
C(132)	0.721(1)	0.285(3)	0.173(1)
C(133)	0.785(1)	0.293(3)	0.194(1)
C(134)	0.810(2)	0.183(3)	0.224(2)
C(135)	0.779(1)	0.082(3)	0.231(1)
C(136)	0.715(2)	0.083(3)	0.211(2)
C(141)	0.568(1)	0.311(3)	0.187(1)
C(142)	0.530(1)	0.380(3)	0.145(1)
C(143)	0.504(2)	0.480(3)	0.175(2)
C(144)	0.513(2)	0.514(4)	0.239(2)
C(145)	0.553(2)	0.442(4)	0.280(2)
C(146)	0.581(2)	0.344(3)	0.253(2)
Cl(S1)	0.5651(7)	−0.196(2)	0.3978(8)
Cl(S2)	0.5642(6)	−0.423(1)	0.4511(6)
C(S)	0.409(2)	0.283(4)	0.551(2)

[a] Atoms of solvent molecule are denoted by S.

as $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{1/2}/L_p$, and the 'ignorance factor' p being set at 0.04. The final values of the agreement indices are also reported in Table 3.

Because of the presence of several ghost peaks around the iridium atoms in the last difference Fourier maps and the poorly defined geometry of some of the ligands, an extra absorption correction (DIFABS) [21] was applied to the full data set after complete isotropic refinement, according to that suggested for strongly absorbing crystals by Demartin *et al.* [22] (min–max transmission factors: 0.84–1.32) (an analogous treatment of the data was applied to **2** and **3** [2]); the R_w factor decreased at this stage from 0.081 to 0.056, and subsequent least-squares refinements showed the overall stereogeometry of the ligands to be chemically sound. Anisotropic thermal parameters were assigned to the Ir, Cu, P and Cl atoms. The hydrogen atom contributions to the scattering factors were neglected. The peaks in the final difference Fourier map were randomly located. The final values of the positional parameters for **1A** are reported in Table 4.

Additional supplementary material comprises anisotropic thermal factors, the list of observed and calculated structure factors and the complete list of bond distances and angles, and is available from the authors.

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