Synthesis, Characterization and Crystal Structures of $[Ir_9H(CO)_{19}]^{4-}$ and $[Ir_{10}(CO)_{21}]^{2-}$

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The base-induced condensation of $[Ir_4(CO)_{12}]$ at room temperature has yielded $[Ir_9(CO)_{20}]^{3-}$ and $[Ir_9H(CO)_{19}]^{4-}$, which both reveal a face-sharing bioctahedral metallic framework; oxidation of $[Ir_9(CO)_{20}]^{3-}$ produced $[Ir_{10}(CO)_{21}]^{2-}$, after addition of a butterfly-capping iridium atom; these clusters have been compared with known compounds of ruthenium, rhodium and iridium, which together model the building-up process of the closed-shell trigonal-bipyramidal polyhedron; step-by-step growth shows irregularities in the number of valence electrons, since the larger clusters require more filled orbitals than predicted by the capping principle.

Formerly, metal clusters containing six or more atoms have been defined as compounds of high nuclearity.[1] Nowadays, following recent developments in this area, clusters with seven to twelve metal atoms are usually considered too small to be included in the high nuclearity series.[2] Nevertheless, owing to their rigid metal skeleton (frequently fragments of close-packed lattices) and their accurate (chemical, spectroscopic and structural) characterization, they represent invaluable tools for bonding analyses,[3] models for nucleation of metallic particles[4,5] and for theoretical predictions on the transition between molecular compounds and bulk metals.[5,6]

Recently, we have isolated and characterized some medium-sized iridium clusters, *viz.* $[Ir_{12}(CO)_{26}]^{2-}$,[7] $[Ir_{12}(CO)_{24}]^{2-}$ (ref. 8) and $[Ir_{14}(CO)_{27}]^{-}$,[9] which partially fill the gap between the cluster chemistry of this metal and that of the neighbouring elements, especially rhodium, for which a wide variety of carbonyl cluster complexes are known. The new species, which are obtained reproducibly and in reasonably high yields, may also be used as starting materials for further investigations. Accordingly, having devised an efficient synthesis of $[Ir_9(CO)_{20}]^{3-}$ **1**,[10] we explored its redox reactivity and observed the formation of further compounds, as discussed below.

We have found that $[Ir_4(CO)_{12}]$ undergoes a base-induced condensation when it is treated with K_2CO_3 in methanol at room temperature. After 60 h a mixture of different clusters is formed, which are separated by precipitation in water with cations of increasing size. The yield of $Cs_3[Ir_9(CO)_{20}]$ (*ca.* 50% of the starting iridium) is substantially higher than that of the redox condensation reported previously (< 10%).[10] A more reduced species, which is still soluble after the addition of CsCl, can be precipitated with tetraalkylammonium salts. The new anion $[Ir_9H(CO)_{19}]^{4-}$ **2**, which constitutes *ca.* 20% of the reaction mixture, may thus be isolated and crystallized as $[NEt_4]_4[Ir_9(\mu\text{-}H)(\mu\text{-}CO)_7(CO)_{12}]\cdot MeCN$ [ν_{CO}(MeCN): 1998w, 1954vs, 1930s, 1744m cm^{-1}; ^1H NMR (CD_3CN, −40 °C): δ 20.7] from MeCN–diisopropyl ether and the solid-state structure determined by X-ray diffraction.† The cluster is exceedingly air sensitive and should be handled only in very concentrated solutions, to reduce possible reactions with solvent impurities. Thus, the oxidation of **2** to $[Ir_9(CO)_{20}]^{3-}$ was facile, but it was impossible to obtain pure $[Ir_9H(CO)_{19}]^{4-}$ by the basic reduction of **1**, since reoxidation always occurred during the work-up.

Clusters **1** and **2** are structurally related as they both contain a face-sharing bioctahedral metal framework. However, although both anions contain seven bridging carbonyls, they span different edges and the overall disposition of the carbonyl ligands differs significantly in the two clusters.[10] In addition, in **2**, a large hole was detected in the space-filling model of ligand distribution over the metal skeleton, which was assigned to the bridging hydride ligand. As shown in Fig. 1, this bridges the

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† Crystal data. $[NEt_4]_4[Ir_9H(CO)_{19}]\cdot MeCN$, $C_{53}H_{84}Ir_9N_5O_{19}$, $M = 2825.08$, monoclinic, space group $P2_1/n$ (no. 14), $a = 13.064(3)$, $b = 23.540(15)$, $c = 22.703(8)$ Å, $\beta = 97.34(3)°$, $U = 6925(9)$ Å^3, $Z = 4$, $D_c = 2.710$ g cm^{-3}, crystal dimensions 0.05 × 0.15 × 0.20 mm, $F(000) = 5128$, μ(Mo-Kα) = 172.26 cm^{-1}, $R = 0.042$ and $R' = 0.035$ for 4160 independent reflections, decay (58% on I) and absorption-corrected reflections having $I > 3\sigma(I)$ (relative maximum, minimum transmission factors: 1.00, 0.28).

$[NMe_3(CH_2Ph)]_2[Ir_{10}(CO)_{21}]$, $C_{41}H_{32}Ir_{10}N_2O_{21}$, $M = 2810.71$, monoclinic, space group $P2_1/c$ (no. 14), $a = 23.990(12)$, $b = 12.763(6)$, $c = 18.653(13)$ Å, $\beta = 111.35(5)°$, $U = 5319(11)$ Å^3, $Z = 4$, $D_c = 3.509$ g cm^{-3}, crystal dimensions 0.05 × 0.05 × 0.25mm, $F(000) = 4920$, μ(Mo-Kα) = 248.93 cm^{-1}, $R = 0.046$ and $R' = 0.043$ for 2792 independent reflections, decay (23% on I) and absorption-corrected reflections having $I > 3\sigma(I)$ (relative maximum, minimum transmission factors: 1.00, 0.23).

For both compounds the intensity data were collected on an Enraf-Nonius CAD4 automated diffractometer (Mo-Kα radiation, λ = 0.710 73 Å) by the ω-scan method, within the limits $3 < \theta < 25°$. The structures were solved by direct methods (SIR92[11]) and Fourier-difference syntheses and refined by full-matrix least squares (SHELX 76[12]) $\{R = \Sigma||F_o| - k|F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - k|F_c|)^2/\Sigma w(|F_o|^2)]^{\frac{1}{2}}$, $w = A/[\sigma^2(F_o) + BF_o{}^2]$, with $A = 1.968$, 2.166 and $B = 0.000\,102$, 0.000 293 for complexes of **2** and **4**, respectively$\}$. The hydride location in **2** was determined using the program HYDEX,[13] but was not included in the refinement. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

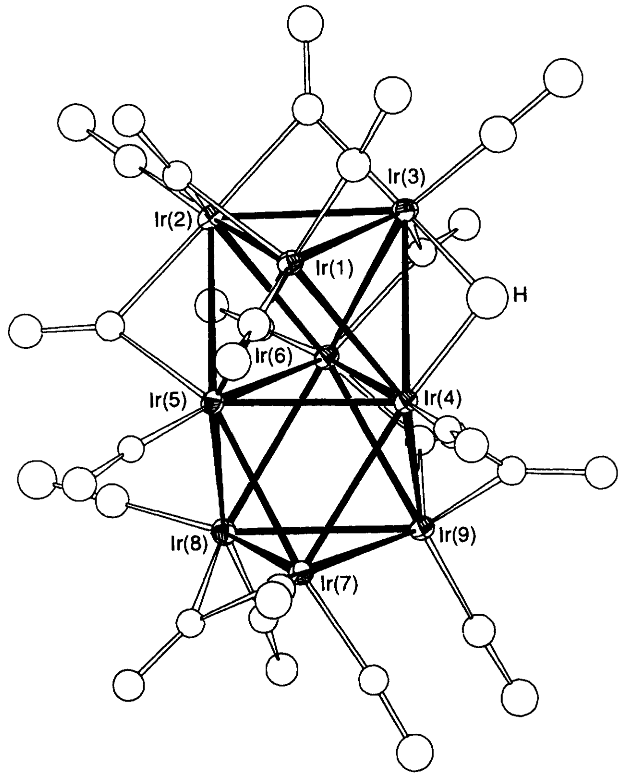

Fig. 1 An ORTEP[14] drawing of the $[Ir_9H(CO)_{19}]^{4-}$ anion, with partial labelling scheme. Relevant bond distances (Å) and angles (°) are: Ir(1)–Ir(2) 2.751(2), Ir(1)–Ir(3) 2.826(2), Ir(1)–Ir(4) 2.812(2), Ir(1)–Ir(5) 2.731(2), Ir(2)–Ir(3) 2.770(2), Ir(2)–Ir(5) 2.729(2), Ir(2)–Ir(6) 2.882(2), Ir(3)–Ir(4) 2.846(2), Ir(3)–Ir(6) 2.798(2), Ir(4)–Ir(5) 2.768(1), Ir(4)–Ir(6) 2.814(2), Ir(4)–Ir(7) 2.815(2), Ir(4)–Ir(9) 2.734(2), Ir(5)–Ir(6) 2.795(2), Ir(5)–Ir(7) 2.719(2), Ir(5)–Ir(8) 2.722(2), Ir(6)–Ir(8) 2.855(2), Ir(6)–Ir(9) 2.765(2), Ir(7)–Ir(8) 2.825(2), Ir(7)–Ir(9) 2.825(2), Ir(8)–Ir(9) 2.827(2); average $Ir–C_t$ 1.80, $Ir–C_b$ 1.99, $C–O_t$ 1.19, $C–O_b$ 1.24, $Ir–C–O_t$ 176 and $Ir–C–O_b$ 136 (t = terminal, b = bridging)

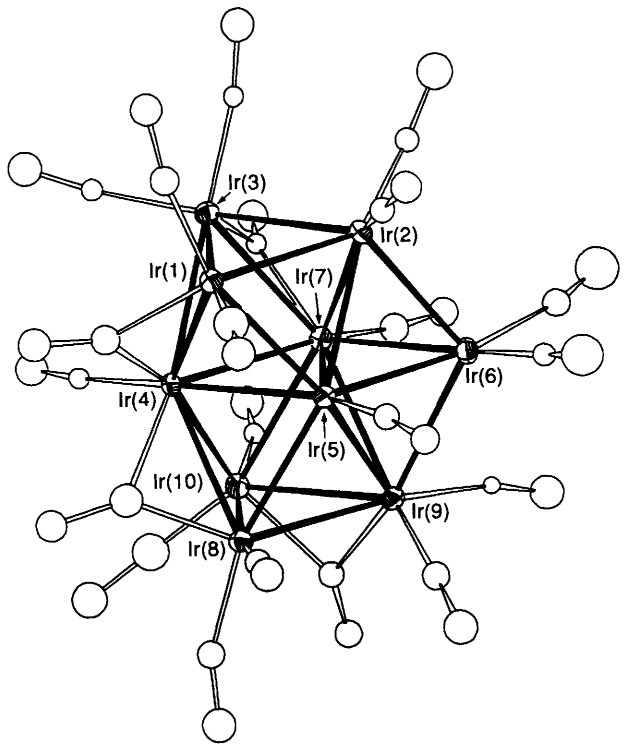

Fig. 2 An ORTEP drawing of the $[Ir_{10}(CO)_{21}]^{2-}$ anion, with partial labelling scheme. Relevant bond distances (Å) and angles (°) are: Ir(1)–Ir(2) 2.812(3), Ir(1)–Ir(3) 2.792(3), Ir(1)–Ir(4) 2.779(3), Ir(1)–Ir(5) 2.710(3), Ir(2)–Ir(3) 2.771(3), Ir(2)–Ir(5) 2.673(3), Ir(2)–Ir(6) 2.611(3), Ir(2)–Ir(7) 2.789(3), Ir(3)–Ir(4) 2.782(3), Ir(3)–Ir(7) 2.810(3), Ir(4)–Ir(5) 2.750(3), Ir(4)–Ir(7) 2.799(3), Ir(4)–Ir(8) 2.763(3), Ir(4)–Ir(10) 2.798(3), Ir(5)–Ir(6) 2.631(3), Ir(5)–Ir(7) 2.696(3), Ir(5)–Ir(8) 2.717(4), Ir(5)–Ir(9) 2.795(3), Ir(6)–Ir(7) 2.703(3), Ir(6)–Ir(9) 2.757(3), Ir(7)–Ir(9) 2.805(3), Ir(7)–Ir(10) 2.772(4), Ir(8)–Ir(9) 2.847(3), Ir(8)–Ir(10) 2.789(3), Ir(9)–Ir(10) 2.783(3); average $Ir–C_t$ 1.85, $Ir–C_b$ 2.03, $C–O_t$ 1.17, $C–O_b$ 1.19, $Ir–C–O_t$ 170 and $Ir–C–O_b$ 137

Ir(3)–Ir(4) edge, which is slightly elongated by the μ-H ligand [2.846(2) Å].

Protonation of **1** yields the dianion $[Ir_9H(CO)_{20}]^{2-}$ **3** {ν_{CO} [tetrahydrofuran (thf)]: 2056w, 2011vs, 1987m, 1956w, 1819w, 1797m cm^{-1}; ^1H NMR ([$^2H_8$]thf, −40 °C): δ −16.5} which is slowly oxidized into $[Ir_{10}(CO)_{21}]^{2-}$ **4**. Neither **3** nor **4** could be obtained pure by this method, since they cannot be easily separated; instead, they cocrystallize in the same lattice and both were found to be present by X-ray analysis, in variable ratios, in crystals of several salts with different cations. Therefore, the oxidation of **1** must be performed with reagents other than H^+, and $[Fe(\eta^5-C_5H_5)_2]^+$, Fe^{III} salts, $[Cu(NCMe)_4]^+$, CCl_4 and even atmospheric oxygen were employed for the preparation of **4** giving comparable yields.* Crystals of the salt $[NMe_3(CH_2Ph)]_2[Ir_{10}(\mu-CO)_4(CO)_{17}]$ [ν_{CO}(thf): 2058w, 2015vs, 1804m cm^{-1}], grown from thf–cyclohexane, were suitable for X-ray analysis.† The metal framework of **4** is also based on a bioctahedron. The tenth iridium atom caps one of the three (lateral) butterfly surfaces, forming a condensed trigonal-bipyramidal cavity (Fig. 2). The same polyhedron is adopted by $[Rh_{10}(CO)_{21}]^{2-}$,[15] which possesses a different stereochemistry of the carbonyl ligands, only 7 out of 21 being terminally bonded. Such metal packing has recently been found for the ruthenium atoms in the mixed metal cluster $[Ru_{20}Cu_6H_4(CO)_{48}Cl_2]^{2-}$.[16] The capping atom is readily displaced from $[Rh_{10}(CO)_{21}]^{2-}$ by addition of halides,[15] with the formation of $[Rh_9(CO)_{19}]^{3-}$.[17] The same reaction was not observed for **4**, since this would generate the as yet unknown, unsaturated $[Ir_9(CO)_{19}]^{3-}$ species.

In contrast to the face-centred cubic (f.c.c.) structure of iridium metal, the ABA sequence of compact layers present in **2** and **4**, is reminiscent of the hexagonal close packed (h.c.p.) framework; this is not altogether surprising as even in iridium clusters of higher nuclearity no f.c.c. sequence has ever been found; however, h.c.p. ($[Ir_{12}(CO)_{26}]^{2-}$)[7] or *mixed* sequence skeletons ($[Ir_{12}(CO)_{24}]^{2-}$ [8] and $[Ir_{14}(CO)_{27}]^-$ [9]) have been structurally characterized.

The nine- and ten-vertex skeletons of **2** and **4** are also related by the capping principle, as predicted by the polyhedral skeletal electron-pair approach.[18] The clusters $[Ir_9H(CO)_{19}]^{4-}$ and $[Ir_{10}(CO)_{21}]^{2-}$ possess 124 and 134 cluster valence electrons, respectively; the difference is accounted for by the (tetra-connected) atom capping a butterfly surface. The clusters $[Ru_{11}H(CO)_{27}]^{3-}$ (146)[19] and $[Ir_{12}(CO)_{24}]^{2-}$ (158 valence electrons),[8] represent the next steps in the capping process, being formed by successive addition of metal atoms to butterfly and triangular surfaces, respectively; however they do not conform to the same electron counting scheme, as they have two extra electrons. This building-up process ideally leads to the closed-shell structure of $[Ir_{14}(CO)_{27}]^-$.[9] The nonanuclear clusters **1**, **2** and **3** do not have the same electron count as the corresponding rhodium complex $[Rh_9(CO)_{19}]^{3-}$ (122 valence

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* In a typical reaction $[PPh_4]_3[Ir_9(CO)_{20}]$ (3.10 mg, 0.094 mmol) was dissolved in MeCN (20 cm^3), then $[Fe(\eta^5-C_5H_5)_2]PF_6$ (54 mg, 0.16 mmol) was added in three portions and allowed to react for 2 h. The solvent was removed *in vacuo* and the residue dissolved in MeOH. A black solid was eliminated by filtration and the crude product crystallized by dropwise addition of water. Crystals were grown from thf–cyclohexane.

† See footnote † on previous page.

electrons)[17] but **4** has the same number of cluster valence electrons as $[Rh_{10}(CO)_{21}]^{2-}$. The lower number of electrons in $[Rh_9(CO)_{19}]^{3-}$ is explained by the stronger interactions in the condensed octahedra which raise the energy of one skeletal orbital of these subunits to an antibonding level.[3,18] Loss of molecular symmetry induced by ligand arrangements can also be envisaged.[10]

Overall, the progressively increasing negative charge causes a lengthening in the average Ir–Ir distances in **4** (2.757 Å), **1** (2.780 Å) and **2** (2.791 Å); the Ir–C and C–O bond distances in **2** and **4** are also affected, in keeping with the reduced π^* back donation n the latter species.

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