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Preliminary communication

SYNTHESIS AND X-RAY CHARACTERIZATION OF THE $[Ir_6(CO)_{15}COEt]^-$ ANIONIC CLUSTER

FRANCESCO DEMARTIN, MARIO MANASSERO, MIRELLA SANSONI,
Istituto di Chimica Generale, Reparto Strutture, via G. Venezian 21, 20133 Milano (Italy)
LUIGI GARLASCHELLI, CARLO RAIMONDI C.,
Dipartimento di Chimica Inorganica e Metallorganica, via G. Venezian 21, 20133 Milano (Italy)
and SECONDO MARTINENGO
Centro CNR Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione, via G. Venezian 21, 20133 Milano (Italy)

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Summary

The reaction of $Ir_6(CO)_{16}$ with a mixture of CO, H_2, and ethylene yields the $[Ir_6(CO)_{15}COEt]^-$ anion, which has been shown by X-ray diffraction to contain an octahedral iridium cluster bearing a σ-bonded acyl group; the arrangement of the 11 terminal and 4 edge-bridging carbonyl groups is different from that found in both the analogous rhodium complex and the parent $Ir_6(CO)_{16}$ carbonyl.

Only a few examples of derivatives of $Ir_6(CO)_{16}$ are known. We have previously reported the synthesis and structure of the anionic carbonyl cluster $[Ir_6(CO)_{15}]^{2-}$ [1] and of the first neutral substituted derivative of $Ir_6(CO)_{16}$, $Ir_6(CO)_{12}[P(OPh)_3]_4$ [2]. As part of a study of the reactivity of $Ir_6(CO)_{16}$ towards nucleophilic ligands, we have isolated a series of derivatives of the general formula $[Ir_6(CO)_{15}X]^-$, (X = H, Cl, Br, I, COEt). In view of current interest in cluster compounds bearing organic groups, we report here the synthesis and X-ray structure of the monoanionic acyl derivative of $Ir_6(CO)_{16}$, the anion $[Ir_6(CO)_{15}COEt]^-$. This cluster compound was prepared in a way similar to that used for the rhodium analogue [3] by stirring at room temperature for 24 h a solution of $Ir_6(CO)_{16}$ in THF containing 1% of water under an atmosphere of CO, H_2 and ethylene in the molar ratio 1/1/2. Crystals of the corresponding tetraphenylphosphonium salt, suitable for X-ray structure analysis, were obtained by slow diffusion of propan-2-ol into the result-

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ing THF solution of the hydronium salt. The IR spectrum in THF solution shows bands at: $\nu(CO)_{term.}$ 2081vw, 2024vs, 2022vs; $\nu(CO)_{bridg.}$ 1812m, 1785m; $\nu(CO)_{acyl}$ 1665w cm^{-1}.

Crystal data: $C_{42}H_{25}Ir_6O_{16}P$, M = 1969.8, dark-red triclinic prisms, space group $P\bar{1}$ (after refinement), a 12.970(3), b 14.461(5), c 12.661(3) Å, α 89.73(3), β 79.58(3), γ 79.15(3)°, U 2293 Å^3, $Z = 2$, D_c 2.85 g cm^{-3}, μ(Mo-K_α) 184.5 cm^{-1}.

Intensity data were collected on a CAD-4 diffractometer, with graphite-monochromated Mo-K_α radiation in the 2θ range 6—50°. The structure was solved by conventional Patterson and Fourier methods and refined using 5290 absorption-corrected reflections having $I \geqslant 3\sigma(I)$. The final full-matrix least-squares refinement led to conventional R and R_w values of 0.033 and 0.039, respectively. Typical e.s.d.'s on single distances are Ir—Ir 0.001, Ir—C 0.015, C—O 0.015 Å.

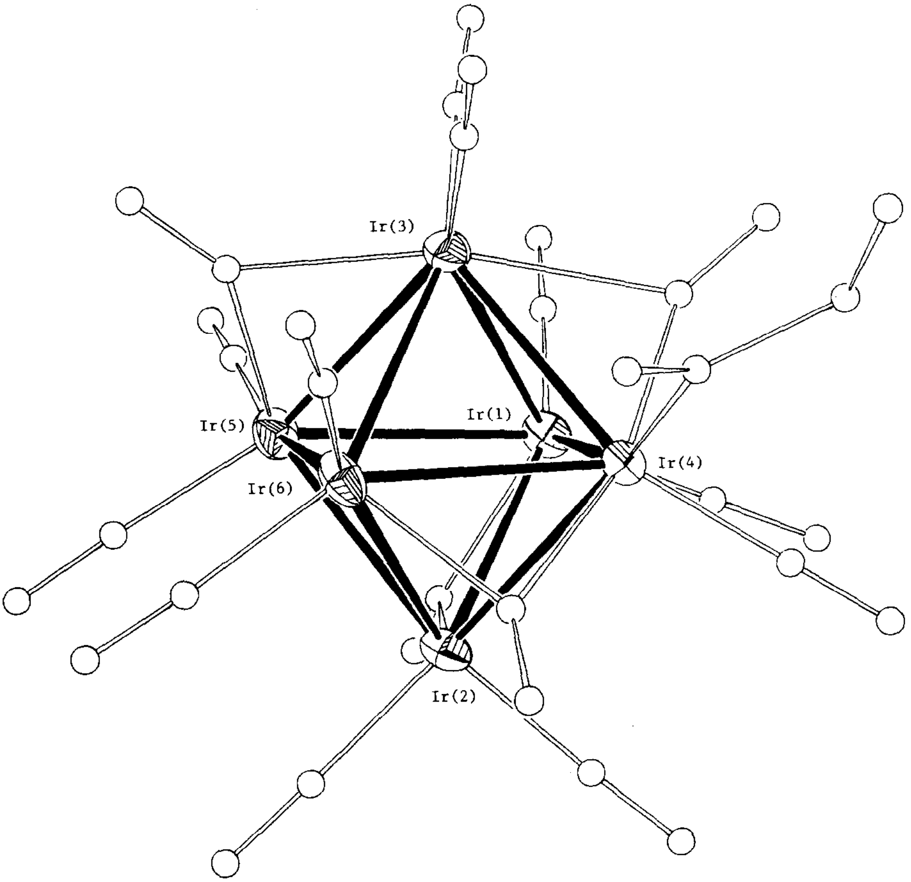

Fig. 1. ORTEP view of the $[Ir_6(CO)_{15}COEt]^-$ anion. Metal—metal bond lengths are: Ir(1)—Ir(2) 2.690(1), Ir(1)—Ir(3) 2.846(1), Ir(1)—Ir(4) 2.870(1), Ir(1)—Ir(5) 2.768(1), Ir(2)—Ir(4) 2.871(1), Ir(2)—Ir(5) 2.776(1), Ir(2)—Ir(6) 2.809(1), Ir(3)—Ir(4) 2.771(1), Ir(3)—Ir(5) 2.760(1), Ir(3)—Ir(6) 2.779(1), Ir(4)—Ir(6) 2.744(1), Ir(5)—Ir(6) 2.794(1) Å.

The anion $[\mathrm{Ir_6(CO)_{15}COEt}]^-$, which does not posses any idealized symmetry element, contains an octahedral cluster of metal atoms with 11 terminal and 4 edge-bridging carbonyl ligands, the acyl group being σ bonded to Ir(4). The two bridging carbonyls bonded to Ir(3) are asymmetric, with the Ir(3)—C distance being the longer in both cases (Ir(3)—$\mathrm{C_{(av.)}}$ 2.216, Ir(4,5)—$\mathrm{C_{(av.)}}$ 2.004 Å). The two remaining bridging carbonyls are symmetric, with an average Ir—C distance of 2.080 Å. Average values for the remaining equivalent dimensions are: Ir—$\mathrm{C_{(term.)}}$ 1.868, C—$\mathrm{O_{(term.)}}$ 1.176 Å, Ir—C—$\mathrm{O_{(term.)}}$ 176.8°. The Ir(4)—$\mathrm{C_{(acyl)}}$ length is 2.078(12) Å, very similar to the Rh—$\mathrm{C_{(acyl)}}$ bond length (2.06(2) Å) in the analogous $\mathrm{(PPh_4)[Rh_6(CO)_{15}COEt]}$ [4].

As a result of the unsymmetrical bonding environment around each iridium atom the Ir—Ir bond lengths vary over the range 2.690—2.871 Å, with a mean value of 2.790 Å (see Caption of Fig. 1). The replacement of a terminal carbonyl of $\mathrm{Ir_6(CO)_{16}}$ by an acyl group, which is approximately normal to the plane defined by atoms Ir(3), Ir(4) and Ir(6), results in a stereochemical distribution of the CO ligands different from that found in both isomers of the parent $\mathrm{Ir_6(CO)_{16}}$ compound, in which the bridging carbonyls are placed either on opposite edges or on opposite faces of the octahedron [5]. A comparison of the structures of $\mathrm{(PPh_4)[Ir_6(CO)_{15}COEt]}$ and $\mathrm{(PPh_4)[Rh_6(CO)_{15}COEt]}$ shows that while the crystal parameters of the two compounds are very similar*, the carbonyl arrangements are different, that in the rhodium complex being very similar to that in the parent $\mathrm{Rh_6(CO)_{16}}$ complex.

The ^{1}H NMR spectrum in $\mathrm{CD_3COCD_3}$ of $\mathrm{(PPh_4)[Ir_6(CO)_{15}COEt]}$ shows the expected pattern for the acylic ethyl group (δ 0.81(t) and 3.03(q) ppm) with the correct intensity ratio relative to the protons of the cation. Further confirmation of the presence of an acyl group comes from the reaction of $\mathrm{(PPh_4)[Ir_6(CO)_{15}COEt]}$ with iodine in anhydrous methanol, which gives the expected methylpropionate.

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*For $\mathrm{(PPh_4)[Rh_6(CO)_{15}COEt]}$: a 12.996(7), b 14.484(7), c 12.748(7) Å, α 89.75(5), β 80.56(5), γ 80.47(5)°.