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Preliminary communication

A NEW TETRAHEDRAL CLUSTER OF IRIDIUM CONTAINING TWO TERMINAL HYDRIDES. SYNTHESIS AND X-RAY STRUCTURE OF DIHYDRIDODECACARBONYL-*tetrahedro*-TETRAIRIDATE(2-)

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Summary

The synthesis of the novel hydridocarbonyl cluster anion $[\text{H}_2\text{Ir}_4(\text{CO})_{10}]^{2-}$ and its characterization by IR, NMR and X-ray analyses are reported. The structure of the anion is similar to that of $\text{M}_4(\text{CO})_{12}$ ($\text{M} = \text{Co}, \text{Rh}$) but with two terminal CO groups replaced by the hydrido ligands. In the metal atom tetrahedron the Ir—Ir bonds *trans* to the H atoms are significantly longer than the others.

The previously known hydridocarbonyl clusters of iridium, $[\text{H}\text{Ir}_4(\text{CO})_{11}]^-$ and $\text{H}_2\text{Ir}_4(\text{CO})_{11}$, were prepared by the reaction of $\text{Ir}_4(\text{CO})_{12}$ with methanolic KOH or metallic sodium in THF [1]. In order to obtain new carbonyl cluster anions of this kind we have studied the reaction of $\text{Ir}_4(\text{CO})_{12}$ with RO^- in ROH ($\text{R} = \text{Me}, \text{Et}$) and the subsequent reaction of the carboalkoxy species $[\text{Ir}_4(\text{CO})_{11}(\text{COOR})]^-$ [2] in alcoholic alkaline hydroxides. Under these conditions, the novel anionic cluster $[\text{H}_2\text{Ir}_4(\text{CO})_{10}]^{2-}$ was obtained along with small amounts of other products which are under investigation. The anion was isolated as the bis(triphenylphosphine)iminium salt and also as the tetraphenylphosphonium salt. The IR spectrum in CH_3CN shows bands at 2020m, 1975vs, 1955vs, 1905m cm^{-1} , due to terminal carbonyls and perhaps Ir—H stretchings, and at 1825w, 1790s, 1755s cm^{-1} , due

to bridging carbonyls. The NMR spectrum in CD_3CN exhibits a hydridic signal at τ 26.15 ppm, and the integration is in agreement with the proposed stoichiometry.

The bis(triphenylphosphine)iminium salt crystallizes as orange-brown monoclinic prisms, space group $P2_1/c$, with a 14.307(3), b 23.657(5), c 23.601(5) Å, β 92.32(5)°. Its structure was solved by Patterson and Fourier methods based on counter data collected on a Philips PW1100 diffractometer, with graphite monochromatized $\text{Mo-K}\alpha$ radiation. A block-matrix least-squares refinement, carried out with 2234 reflections having $\sigma(I)/I \leq 0.10$, in which the Ir atoms have been assigned with anisotropic thermal factors, has led to a current R value of 0.040.

The anion geometry is shown in Fig. 1 and the principal bond parameters are listed in Table 1. The metal atoms are disposed tetrahedrally (mean Ir—Ir distance 2.76 Å) and the idealized symmetry of the whole anion is C_s , the mirror passing through atoms Ir(1) and Ir(2). Of the ten carbonyl ligands, seven are terminal (mean Ir—C and C—O 1.80 and 1.21 Å): three are bonded to the apical metal atom Ir(1), two to Ir(2) and one each to Ir(3) and Ir(4). The three remaining carbonyls are double bridging on the three edges of the basal triangle and lie approximately in its plane. Two of them, on edges Ir(2)—Ir(3) and Ir(2)—Ir(4), are markedly asymmetric (Ir(2)—C(mean) 2.12 Å, Ir(3,4)—C(mean) 1.90 Å). A similar asymmetry has been observed in many polynuclear carbonyl compounds, such as, for instance, $[\text{FeCo}(\text{CO})_8]^-$ [3], $[\text{Rh}_4(\text{CO})_{11}]^{2-}$ [4], $[\text{Rh}_6(\text{CO})_{15}\text{I}]^-$ [5], $[\text{Ir}_4(\text{CO})_{11}\text{Br}]^-$ [6], and many others. It can be ascribed principally to charge equalization and this will be discussed in more detail later [6].

The overall disposition of the carbonyl ligands resembles that found in $\text{Co}_4(\text{CO})_{12}$ [7] and in $\text{Rh}_4(\text{CO})_{12}$ [8] with two terminal carbonyls missing in the basal triangle. It gives rise, therefore, to two free coordination sites on atoms Ir(3) and Ir(4), thus providing indirect evidence for the location of the two hydrido ligands (see dashed lines in Fig. 1). The presence of two terminal hydrides is unusual in this type of compound, and may be associated with the low steric requirement of the limited number of carbonyl groups.

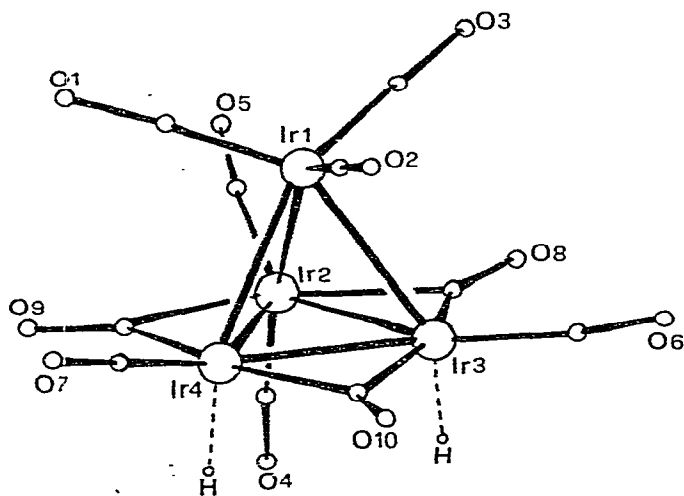


Fig. 1. A view of the anion $[\text{H}_2\text{Ir}_4(\text{CO})_{10}]^{2-}$ with the postulated hydridic hydrogen atoms.

TABLE 1

BOND DISTANCES AND ANGLES IN THE ANION $[\text{H}_2\text{Ir}_4(\text{CO})_{10}]^{2-}$

Distances (Å)		Angles (deg.)	
Ir(1)—Ir(2)	2.763(2)	Ir—Ir(1)—C(<i>trans</i>) ^a	145
Ir(1)—Ir(3)	2.802(2)	Ir—Ir(1)—C(<i>cis</i>) ^a	91
Ir(1)—Ir(4)	2.802(2)	Ir(1)—Ir(2)—C(5)	92(1)
Ir(2)—Ir(3)	2.713(2)	Ir(1)—Ir(3)—C(6)	116(1)
Ir(2)—Ir(4)	2.703(2)	Ir(1)—Ir(4)—C(7)	110(1)
Ir(3)—Ir(4)	2.716(2)	Ir(1)—Ir(2)—C(4)	170(1)
Ir(1)—C(1)	1.80(4)	Ir(3,4)—Ir(2)—C(4) ^a	110
Ir(1)—C(2)	1.80(4)	Ir(3,4)—Ir(2)—C(5) ^a	137
Ir(1)—C(3)	1.77(3)	C(4)—Ir(2)—C(5)	98(2)
Ir(2)—C(4)	1.85(4)	Ir(2,4)—Ir(3)—C(6) ^a	149
Ir(2)—C(5)	1.82(4)	Ir(2,3)—Ir(4)—C(7) ^a	147
Ir(3)—C(6)	1.78(4)	Ir(2)—C(8)—Ir(3)	84(1)
Ir(4)—C(7)	1.75(3)	Ir(2)—C(8)—O(8)	131(2)
C—O(<i>term.</i>) ^a	1.20	Ir(3)—C(8)—O(8)	145(3)
Ir(2)—C(8)	2.12(3)	Ir(2)—C(9)—Ir(4)	86(2)
Ir(3)—C(8)	1.95(3)	Ir(2)—C(9)—O(9)	128(3)
Ir(2)—C(9)	2.12(4)	Ir(4)—C(9)—O(9)	145(3)
Ir(4)—C(9)	1.86(4)	Ir(3)—C(10)—Ir(4)	83(1)
Ir(3)—C(10)	2.06(3)	Ir(3)—C(10)—O(10)	137(3)
Ir(4)—C(10)	2.04(3)	Ir(4)—C(10)—O(10)	139(3)
C—O(<i>bridg.</i>) ^a	1.23		

^a Mean value.

The mean value of the metal—metal bond length (2.76 Å) is influenced by the presence of two very long distances (mean 2.80 Å) *trans* to the hydridic hydrogen atoms, whereas the mean of the remaining four interactions (2.73 Å) is comparable with the mean values observed in $\text{Ir}_4(\text{CO})_{12}$ (2.68 Å) [9] and, especially, in $\text{Ir}_4(\text{CO})_{9-10}(\text{PPh}_3)_{3-2}$ (2.73 Å) [10]. The two long Ir—Ir bonds are clearly a consequence of a structural *trans*-influence of the hydrido ligands, a situation which has not previously been observed in transition metal cluster compounds.

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