

Preliminary communication

NEW TETRAHEDRAL CLUSTER COMPOUNDS OF IRIDIUM. SYNTHESIS OF THE ANIONS $[\text{Ir}_4(\text{CO})_{11}\text{X}]^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}, \text{SCN}$) AND X-RAY STRUCTURE OF $[\text{PPh}_4][\text{Ir}_4(\text{CO})_{11}\text{Br}]$

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Summary

$[\text{Ir}_4(\text{CO})_{11}\text{X}]^-$ anions are obtained by reaction of halide and pseudo-halide ions with $\text{Ir}_4(\text{CO})_{12}$. X-ray determination of the structure of $[\text{Ir}_4(\text{CO})_{11}\text{Br}]^-$ shows that the carbonyl arrangement differs from that of the parent $\text{Ir}_4(\text{CO})_{12}$, and is similar to that known for $\text{Co}_4(\text{CO})_{12}$; one terminal CO group in the basal $\text{M}_3(\text{CO})_9$ moiety is replaced by the bromide ligand, and two of the bridging CO groups become markedly asymmetric.

The known substituted derivatives of $\text{Ir}_4(\text{CO})_{12}$ mainly contain phosphorus donor ligands [1]. We have now studied the reaction with halides and pseudo-halides, which give the new species $[\text{Ir}_4(\text{CO})_{11}\text{X}]^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}, \text{SCN}$). These were obtained by refluxing for 3–4 h a stirred suspension of $\text{Ir}_4(\text{CO})_{12}$ in anhydrous THF, in the presence of a large excess (molar ratio 1/5) of the appropriate nucleophile. The compounds were obtained in reasonable yields when quaternary ammonium and phosphonium salts were used as the entering nucleophiles. The IR spectra (in THF) of these anions show the formation of edge bridging carbonyls, as previously observed for PR_3 substitution; for instance, $[\text{Ir}_4(\text{CO})_{11}\text{Br}]^-$ exhibits, in the CO stretching region, the following bands: 2065m, 2030vs, 1885w and 1835s cm^{-1} .

The structure of $[\text{Ir}_4(\text{CO})_{11}\text{Br}]^-$, determined by X-ray diffraction*, is illus-

*The salt $[\text{PPh}_4][\text{Ir}_4(\text{CO})_{11}\text{Br}]$ gives orange orthorhombic crystals, space group $P2_1 2_1 2_1$ (No. 19), with cell constants a 13.276(3), b 18.347(4) and c 16.041(4) Å. The structure was solved by Patterson and Fourier methods, using 2682 independent counter data, and was refined by block-matrix least-squares assigning anisotropic thermal factors to the Ir, Br and P atoms. The phenyl groups of the cation were refined rigidly. The current conventional R value is 0.059.

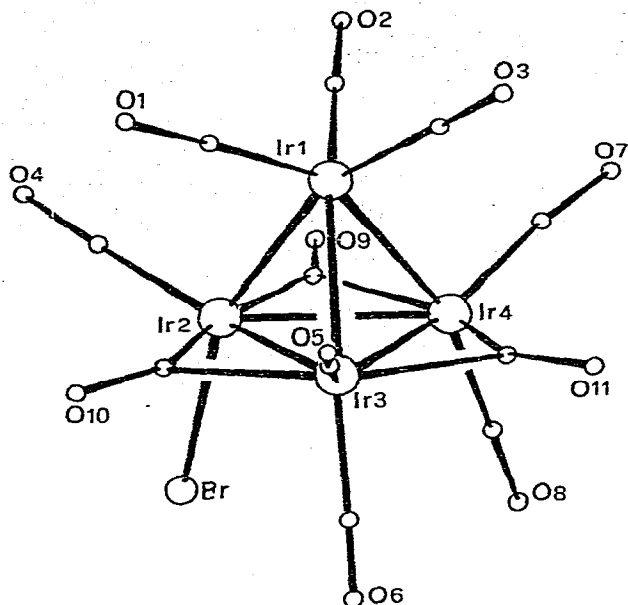


Fig. 1. A view of the anion $[\text{Ir}_4(\text{CO})_{11}\text{Br}]^-$. The Ir—Ir bond distances have the following values: 1—2 2.676, 1—3 2.704, 1—4 2.707, 2—3 2.735, 2—4 2.745 and 3—4 2.695 Å (standard deviations 0.002 Å)

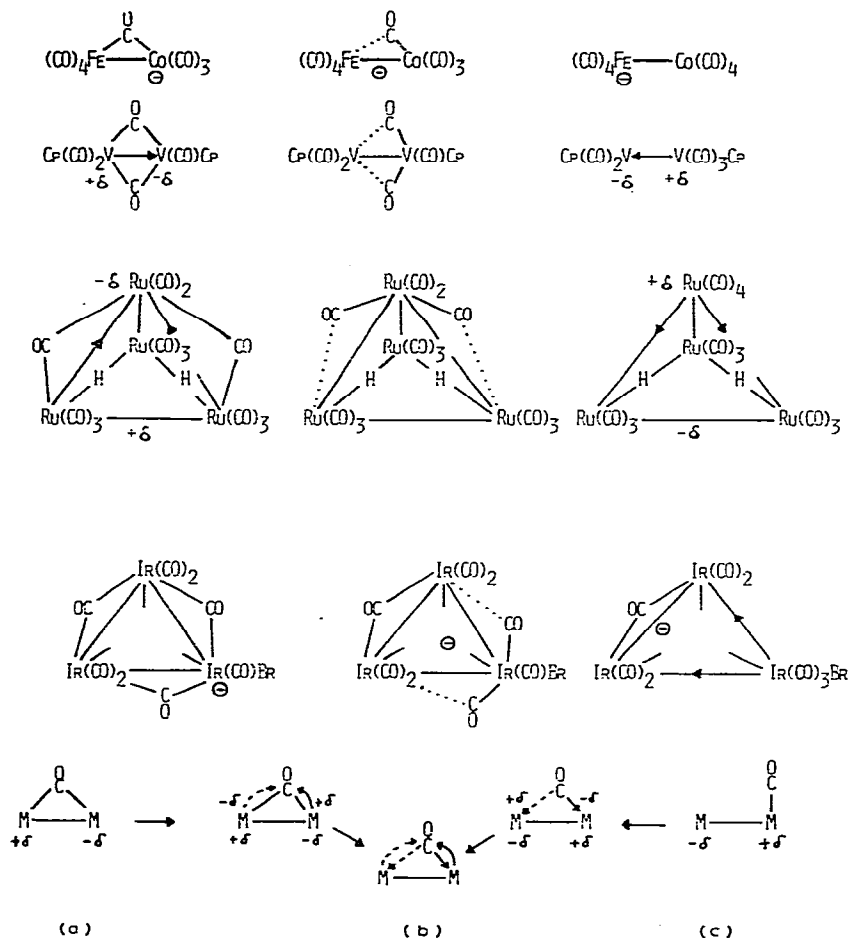
trated in Fig. 1. The anion contains a tetrahedral cluster bearing eight terminal and three edge bridging carbonyl groups; the bromide atom is terminally bonded. The ligand stereochemistry is of the type present in $\text{Co}_4(\text{CO})_{12}$ [2] and in $\text{Rh}_4(\text{CO})_{12}$ [3] with one of the terminal CO groups in the basal $\text{M}_3(\mu\text{-CO})_3(\text{CO})_6$ moiety substituted by the halide ligand.

The Ir—Ir distances have a mean value, 2.710 Å, similar to the corresponding mean values in $\text{Ir}_4(\text{CO})_{12}$ (2.68 Å) [4] and in $\text{Ir}_4(\text{CO})_{9-10}(\text{PPh}_3)_{3-2}$ (2.73 Å) [5]. The small distortions in the metal atom cluster are such as to conform to the idealized C_s symmetry of the whole anion.

The Ir(2)—Br bond length (2.574(4) Å) is somewhat longer than the sum of the covalent radii (ca. 2.50 Å); it is intermediate between the values of the two non-equivalent Ir—Br bonds in $\text{Ir}(\text{B}_5\text{H}_8)\text{Br}_2(\text{CO})(\text{PMe}_3)_2$ (2.516(1) and 2.638(1) Å) [6]. The Ir—C and C—O bonds for the terminal carbonyl ligands have mean values of 1.86 and 1.15 Å.

An interesting feature of the structure is the marked asymmetry of the two edge bridging CO groups bound to Ir(2), the metal atom bearing the halide ligand. For these carbonyl groups the Ir(2)—C bonds (mean 1.97 Å) are distinctly shorter than the Ir(3,4)—C bonds (mean 2.24 Å). The third CO bridge shows only a very small, though significant, asymmetry (Ir—C 2.03 and 2.10 Å).

Generally charge equalization is believed to be the driving force for the presence of asymmetric bridging carbonyls between non equivalent metal atoms [7, 8]. We feel, however, that the present analysis is more useful and complete. The observed asymmetry is clearly an intermediate state between the situation in which the CO groups form symmetric bridges (a) and the situation (c) in which there is attachment through one metal atom only; both of these agree with the noble gas formulation (Scheme 1). Therefore, as shown in Scheme 1,



Scheme 1. The examples cited here are reported in refs. 9, 10, 11 and in this work, respectively.

an asymmetric bridge may be considered as a terminal carbonyl deformed towards the neighbour atom negatively charged, (c) \rightarrow (b), or as a symmetric bridge deformed towards the more negatively charged metal atom, (a) \rightarrow (b). The first model may be rationalized by assuming a relative predominance of donation in terminal carbonyls, which is formally accompanied by a displacement of the negative charge through the metal-metal bond, while the second model is based on predominant back-donation, with a consequent transfer of the negative charge from the exceedingly negative metal to the other one via the CO. Both models result in the same situation (b) in which essentially stronger σ and π bonds give rise to the shorter M-C distance, and they have been arbitrarily separated only in order to allow a simple representation. Other species which can be subjected to the same treatment are $[Rh_4(CO)_{11}]^{2-}$ [12], $[Rh_6(CO)_{15}I]^-$ [13] and $[H_2Ir_4(CO)_{10}]^{2-}$ [14].

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References

- 1 P. Chini and B.T. Heaton, *Topics Curr. Chem.*, 71 (1977) 1.
- 2 C.H. Wei, G.R. Wilkes and L.F. Dahl, *J. Amer. Chem. Soc.*, 89 (1967) 4792.
- 3 C.H. Wei, *Inorg. Chem.*, 8 (1969) 2384.
- 4 G.R. Wilkes, Ph.D. Thesis, University of Wisconsin, Madison, 1965.
- 5 V.G. Albano, P.L. Bellon and V. Scatturin, *Chem. Comm.*, (1967) 730.
- 6 M.R. Churchill and J.J. Hackbarth, *Inorg. Chem.*, 14 (1975) 2047.
- 7 F.A. Cotton and J.M. Troup, *J. Amer. Chem. Soc.*, 96 (1974) 1233; F.A. Cotton, *Progress Inorg. Chem.*, 21 (1977) 1 and refs. therein.
- 8 M.R. Churchill and M.V. Veidis, *J. Chem. Soc. A*, (1971) 2170; (1971) 2995.
- 9 H.B. Chin, M.B. Smith, R.D. Wilson and R. Bau, *J. Amer. Chem. Soc.*, 96 (1974) 5285.
- 10 F.A. Cotton, B.A. Frenz and L. Kruczynski, *J. Amer. Chem. Soc.*, 95 (1973) 951.
- 11 D.B.W. Yawney and R.J. Doedens, *Inorg. Chem.*, 11 (1972) 838.
- 12 V.G. Albano, G. Ciani, A. Fumagalli, S. Martinengo and W.M. Anker, *J. Organometal. Chem.*, 116 (1976) 343.
- 13 V.G. Albano, P.L. Bellon and M. Sansoni, *J. Chem. Soc. A*, (1971) 678.
- 14 G. Ciani, M. Manassero, V.G. Albano, F. Canziani, G. Giordano, S. Martinengo and P. Chini, *J. Organometal. Chem.*, in press.