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Preliminary communication

PREPARATION AND X-RAY CRYSTAL AND MOLECULAR STRUCTURE OF μ-SULFURDIOXIDEBIS(HYDRIDODICARBONYLTRIPHENYLPHOSPHINEIRIDIUM)

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Summary

The preparation and the spectra of $Ir_2(CO)_4(PPh_3)_2(SO_2)_2$ and of the title compound are reported; in the molecular structure of the latter, determined by X-ray crystallographic analysis, there is a relatively long Ir—Ir bond which is accounted for in terms of the acidic nature of SO_2.

When a benzene solution of $Ir_2(CO)_6(PPh_3)_2$ [1], is treated with SO_2 at room temperature, a pale yellow compound is obtained, whose analytical data and molecular weight agree with the formula $Ir_2(CO)_4(PPh_3)_2(SO_2)_2$ (I). The IR spectrum of I in Nujol displays the frequencies ν(CO), 2095, 2059, 2048, 2028; $\nu(SO)_{asym.}$ 1223, 1209; $\nu(SO)_{sym.}$ 1064, 1051 cm^{-1}. When hydrogen is bubbled through a solution of (I) at room temperature a colourless compound is obtained which by analyses is $[IrH(CO)_2(PPh_3)]_2SO_2$ (II). The IR spectrum in Nujol shows the bands ν(CO) 2025, 2020, 2003; ν(IrH) 2127; δ(IrH) 840, 815; $\nu(SO)_{asym.}$ 1190, 1177; $\nu(SO)_{sym.}$ 1046, 1037 cm^{-1}. The band at 2127 cm^{-1} can be assigned to the Ir—H stretching by comparing the spectrum of II with that of the corresponding deuteride whose Ir—D stretching is found at 1500 cm^{-1}.

The crystal and molecular structures of compounds I and II are presently under investigation; preliminary results for II are reported here. Crystal data. $C_{40}H_{32}Ir_2O_6P_2S$, M = 1087.1, monoclinic; a 14.80(1), b 16.22(1), c 16.56(1) Å, β 107.67(5)°; D_m (flotation) 1.88 g cm^{-3}; Z = 4, D_c 1.906; space group $C2/c$ (no. 15).

A total of 2031 independent reflections were measured by counter method with Mo-K_α radiation (λ 0.7107 Å) monochromatized on graphite. The structure solved by Patterson and Fourier methods, is being refined by full matrix least squares; the present R is 0.035. Exhaustive refinement will eventually allow the positions of the hydride ions to be determined.

The crystal consists of discrete molecules possessing crystallographic sym-

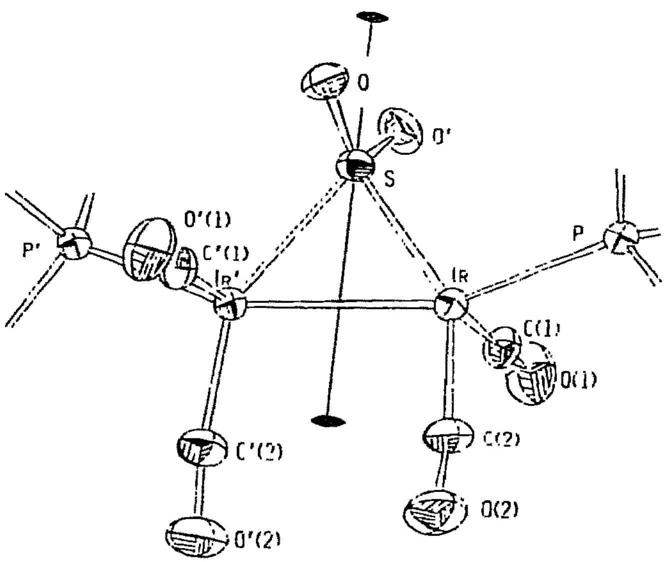

Fig. 1. ORTEP view of a molecule of the title compound (phenyl rings and hydrido ligands have been omitted). Relevant bond distances (Å) and angles (deg.) are: Ir—Ir', 2.759(2); Ir—S, 2.313(3); Ir—P, 2.309(3); Ir—C(1), 1.94(1); Ir—C(2), 1.90(1); C(1)—O(1), 1.12(1); C(2)—O(2), 1.13(1); Ir'—Ir—S, 53.4(1); Ir—S—Ir', 73.1(1); S—O, 1.457(7); O—S—O', 113.7(2).

metry C_2; the sulfur atom lies on the two-fold axis. An overall view of the molecule is shown in Fig. 1. Each iridium atom is at the centre of a distorted octahedron whose apices are occupied by the other iridium and by atoms S, P, C(1), C(2) and H; the latter, not shown, is postulated at the apex *trans* to C(1). The mutually *trans* H^- and CO ligands will destabilize each other [2]; we observe a complicated PMR spectrum which would not be expected for the symmetric structure we find, which is an indication that in solution a different isomer of II is stable.

A naïve description of the electronic structure in II, as adopted for other binuclear cluster complexes containing a bridging SO_2 molecule [3, 4] involves the donation of one electron pair of sulfur to the metal atoms: in each $IrH(CO)_2(PPh_3)$ moiety the metal achieves the inert gas configuration by accepting two electrons, one from sulfur and one from the other metal atom. However, SO_2 is known to behave as a Lewis acid towards mononuclear rhodium and iridium complexes [5] and towards certain cluster molecules [6] as it does towards halide ions and ligands [7].

An important feature which accompanies the presence of bridging SO_2 in a binuclear cluster complex is the lengthening of the M—M bond in comparison with molecules where, in absence of such a bridge, a formal covalent bond connects the two metal atoms. The Ir—Ir distance observed here, 2.759(2) Å. is longer than those observed in $Ir_4(CO)_{12}$, 2.68 Å [8], in $Ir_4(CO)_{12-m}(PPh_3)_m$, 2.72 Å [9], and in $Ir_2(NO)_4(PPh_3)_2$, 2.717 Å [10]. Further, the Fe—Fe distances in $Fe_2(CO)_8(SO_2)$, 2.717 Å [3] and in $Fe_2(C_5H_5)_2(CO)_3(SO_2)$, 2.591 Å [4] are both longer than the distances of 2.50-2.53 Å reported for several Fe—Fe bonds in absence of SO_2 bridges [11]. This elongation can be accounted for if the acidic character of sulfur dioxide is taken into account; in this molecule, the acceptor orbital is the lowest π^* orbital, mainly localized on sulfur, which results from the out-of-phase overlap of three p orbitals [12]. In the present case and i the two Fe_2 complexes cited above, which also possess two-fold symmetry, two suitable metal orbitals (one for each metal atom) and the π^* orbital form a basis for a $A + 2B$ representation of group C_2; the A orbital will be M—M bonding an M—S non-bonding and one B orbital will be M—M anti-bonding and M—S bondi If both these orbitals are filled (the remaining B orbital is totally anti-bonding) one must expect: (i) the M—M bond to be relatively long and (ii) since a π^* orbital of SO_2 is implied which is slightly O—O bonding, the S—O distance to be longer and the O—S—O angle to be smaller than in free SO_2 (cf. the data in the figure caption with the values of 1.43(1) Å and 119.0(5)° observed in gaseous S [13].

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