

### Preliminary communication

## $\{[\text{Ir}(\text{CO})_2\text{PPh}_3]_2-\mu\text{-HC}_2\text{Ph}\}$ : AN ALKYNE DERIVATIVE OF $[\text{Ir}(\text{CO})_3\text{PPh}_3]_2$

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### Summary

The reaction of  $[\text{Ir}(\text{CO})_3\text{PPh}_3]_2$  with phenylacetylene in boiling  $\text{CH}_2\text{Cl}_2$  yields the dinuclear iridium complex  $\{[\text{Ir}(\text{CO})_2\text{PPh}_3]_2-\mu\text{-HC}_2\text{Ph}\}$ . The molecule has an approximate  $C_s$  symmetry and contains a *quasi*-tetrahedral moiety  $\text{Ir}_2\text{C}_2$  involving two alkyne carbon atoms; the C–C distance in the  $\mu$ -bonded acetylenic ligand 1.412(17) Å is the longest ever observed in dimetal- $\mu$ -alkyne complexes.

We are presently studying the products of reactions of substituted acetylenes with  $[\text{Ir}(\text{CO})_3\text{PPh}_3]_2$  (I) [1] and report below preliminary results on  $\{[\text{Ir}(\text{CO})_2\text{PPh}_3]_2-\mu\text{-HC}_2\text{Ph}\}$  (II). This compound is obtained in a yield of ca. 40% when I is treated for about 5 h with phenylacetylene (molar ratio 1/2) in boiling  $\text{CH}_2\text{Cl}_2$  and can be precipitated out by adding ethanol to the reaction mixture. Crystals suitable for diffraction studies can be obtained by slow diffusion of ethanol into a solution of II in  $\text{CH}_2\text{Cl}_2$ .

*Analytical, spectroscopic and crystal data.* Found: C, 51.10; H, 3.20; P, 5.28.  $\text{C}_{48}\text{H}_{36}\text{Ir}_2\text{O}_4\text{P}_2$  ( $M = 1123.18$ ); calcd.: C, 51.33; H, 3.23; P, 5.52%; IR bands:  $\nu(\text{CO})$  2000(s), 1970(ms), 1950(s), 1930(m)  $\text{cm}^{-1}$ ; yellow triclinic prisms, space group  $P\bar{1}$ ,  $a$  18.491(5),  $b$  13.644(4),  $c$  9.901(4) Å,  $\alpha$  114.81(2),  $\beta$  88.66(4),  $\gamma$  101.06(3)°,  $V$  2221 Å<sup>3</sup>,  $D_m$  1.75(2)  $\text{g cm}^{-3}$ ,  $Z = 2$ ,  $D_c$  1.68  $\text{g cm}^{-3}$  \*.

The structure, solved by inspection of Patterson and Fourier syntheses, was refined by block diagonal least-squares method using 4877 independent reflections, collected with graphite-monochromated Mo- $K_\alpha$  radiation, having  $I \geq$

\*The compound actually crystallizes with some solvent ( $\text{CH}_2\text{Cl}_2$ ) which, however, is heavily disordered and cannot be refined. The ratio between the complex molecule and the solvent is about 2/1 as can be seen from  $D_m$ , which has a value intermediate between that reported here, computed without solvent, and that computed for a molar ratio 1/1, the latter being  $D_c = 1.80 \text{ g cm}^{-3}$ .

$3\sigma(I)$ , with phenyl rings of the phosphine ligands constrained to  $D_{6h}$  symmetry (C—C 1.392 Å). Final reliability indices are  $R = 0.037$  and  $R_w = 0.048$ . In the final least squares cycles the contribution of all the hydrogen atoms was included; the position of the hydrogen atom of the alkyne ligand was detected in a difference Fourier map and refined by assigning it a fixed thermal factor.

The structure of II, which seems to be the first example of alkyne derivative of a dinuclear iridium compound, is shown in Fig. 1. The crystal consists of a normal packing of such molecules with no unusual intermolecular contacts. The figure clearly shows an approximate  $C_s$  symmetry with the mirror plane passing through the midpoint of the Ir—Ir bond and containing the

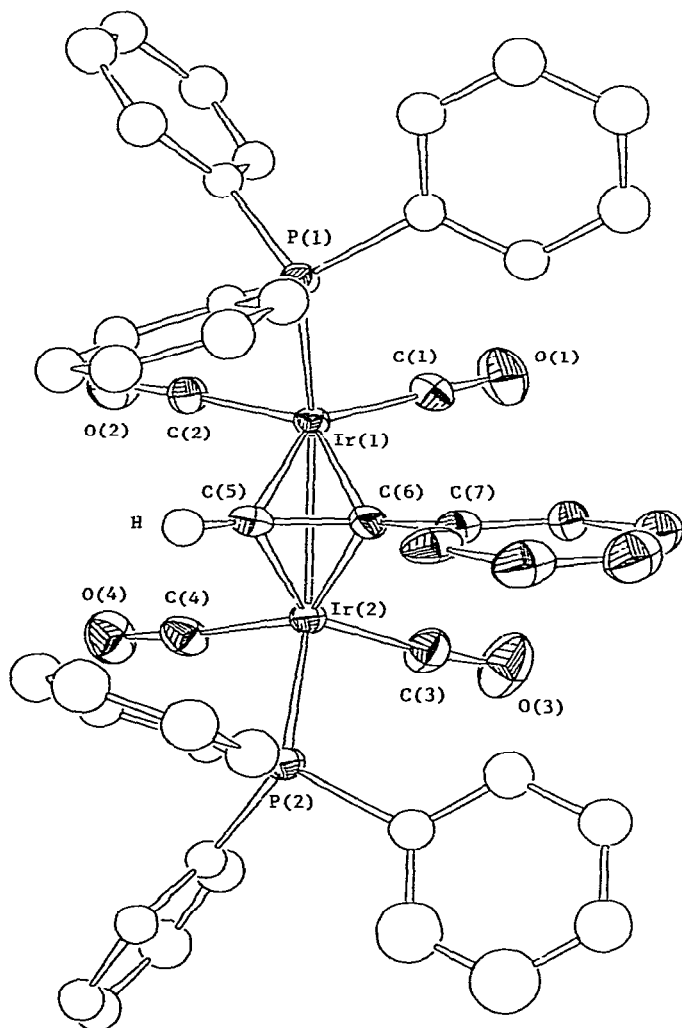


Fig. 1. ORTEP view of  $\{[\text{Ir}(\text{CO})_2\text{PPh}_3]_2 \cdot \mu\text{-HC}_2\text{Ph}\}$ . Relevant distances and angles within the molecule are: Ir(1)—Ir(2) 2.691(1), Ir(1)—P(1) 2.320(2), Ir(2)—P(2) 2.319(3), mean Ir—C(carbonyl) 1.902(38), mean C—O 1.146(27), mean Ir—C(alkyne) 2.118(7), C(5)—C(6) 1.412(17), C(5)—H 0.98(13) Å; C(6)—C(5)—H 147.4(6.4), C(5)—C(6)—C(7) 137.1(1.1)°.

alkyne ligand. Curiously, this symmetry involves the conformation of the  $\text{PPh}_3$  ligands. Each metal atom has a distorted octahedral coordination: an equatorial plane is defined by two carbonyl groups and the  $\mu$ -alkyne ligand, a phosphine group and the other metal atom being in the apical positions. The quasi-tetrahedral moiety  $\text{Ir}_2\text{C}_2$  possesses  $C_{2v}$  symmetry, the four bonds from iridium atoms to the acetylenic carbon atoms being equal within one e.s.d. The Ir(1)—Ir(2) bond length of  $2.691(1)$  Å, agrees with the value of  $2.737(\pm)$  recently found in  $[\text{Ir}(\text{CO})_2\{\text{C}_4(\text{CO}_2\text{Et})_4\text{Ir}(\text{CO})_2(\text{PPh}_3)\}]$  [2], and with a number of values found in di- and polynuclear iridium compounds [3]. The C—C bond length,  $1.412(17)$  Å, in the alkyne ligand seems to be the longest ever observed in  $\text{M}_2-\mu-(\text{R}^1\text{C}\equiv\text{CR}^2)$  complexes [4–8].

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